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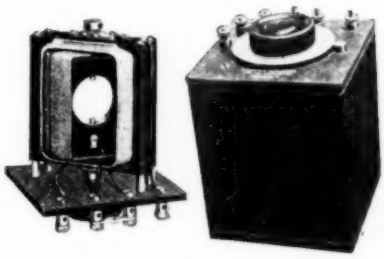

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THE DIFFRACTION OF X-RAYS IN ORGANIC MIXTURES

By Alfred Wesley Meyer
University of Iowa

(Received July 13, 1931)

Abstract

An examination was made by an x-ray diffraction ionization method of the following mixtures: ethyl alcohol-methylcyclohexane, butyl alcohol-ortho-dimethylcyclohexane, quinoline-phenol, paraldehyde-cyclohexane, tetranitromethane-cyclohexane, and phenol-water. All of these mixtures are totally miscible, except the last, phenol-water, which is totally miscible at higher temperatures and is an emulsion in some proportions at ordinary temperatures. In all cases of solutions the diffraction exhibits a single major peak which has an angular position between the positions of the peaks of the constituents and shifts directly with the concentration but in general not in a linear manner. There is in some cases definite indication of the existence of secondary peaks corresponding to those found in the pure constituents but these also shift. In the single case examined of an emulsion, the major peaks of both constituents were found and the intensity of each varied directly with the concentration of that constituent. The results indicate that in a solution there exists a single type of cybotactic group and that the molecules of both constituents enter this formation. The length of the most probable space periodicity in the group depends upon the proportion of the liquids involved. The emulsion contains two types of cybotactic groups corresponding to the two constituent liquids. These conclusions suggest a very fundamental differentiation between solutions and nonsolutions. This differentiation between solutions and nonsolutions does not depend upon the fineness of the separation of either liquid. A solution exists when and only when the components, instead of having their individual space molecular groupings, conspire to form a single type of cybotactic group. With this description, the nature of a solution has a similarity to that of a crystal and has a definite concept.

Introductions

VARIOUS theories have been set forth to interpret the diffraction of x-rays by liquids. Reviews of the literature are presented elsewhere.[1] The conception of Stewart[2] which the present paper corroborates, seems to meet with increasing confirmation. In this the molecules of the liquid are thought of as having throughout a high probability of orderly grouping, with the result that at any moment the liquid is densely populated with small regions of orderly groupings capable of producing definite coherence in x-ray diffraction. The periodicities are not the same throughout any group at any instant,

[1] Good, Helvetica Acta, **III** 205 (1930).
[2] Stewart, Chem. Reviews **6**, 483 (1929).

but follow a probability distribution. The result is, that, instead of giving sharp halos as do powdered crystals, the liquids have diffraction bands with fairly well defined maxima. While there are no definite boundaries to these centers of most orderly arrangement, and while any one group does not retain its identity, yet it is evident that the groupings are significant in any consideration of the nature of a liquid or of its physical characteristics.

The ten pure liquids which were used in mixtures in this investigation have been examined by recent authors.[3]

The halo was first obtained in mixtures of liquids by Wyckoff[4] who investigated mixtures of benzene and carbon tetrachloride, water and glycerol, and methylene iodide and carbon tetrachloride. He concluded that the halos of mixtures are composites of the halos of the members. This is in direct disagreement with the present contribution as well as the experiments of others.

Krishnamurti[5] has investigated a large number of mixtures. He separates mixtures into two classes, (1) those which are totally miscible and which will not separate upon the addition of sodium chloride, and (2) those partially miscible and those which are totally miscible both of which will separate upon addition of sodium chloride. The halos produced by mixtures of the first class are different from those of either member, the peak lying somewhere between those of the components, varying with composition, The diffraction produced by mixtures of the second class consists of the halos of the members, agreeing with Wyckoff. Krishnamurti interprets the results according to the Raman and Ramanathan theory which requires no regular spacing of the molecules, but in later papers he leans pretty strongly toward Stewart's theory. It is to be borne in mind that the former theory shows that there would be halos even with symmetrical molecules, whereas the latter includes a general asymmetry of the molecules. There is no contradiction, but a difference in emphasis.

[3] Note: (numbers following references refer to liquids in Table 1).
Keesom, Physics, 118 (1922); 10, 1.
Keesom and Smedt, Proc. Roy. Soc., Amsterdam **25,** 118 (1922); 10, 1.
Keesom and Smedt, Proc. Roy. Soc., Amsterdam **26,** 118 (1923); 10, 1.
De Smedt, Bull J. Belg. **10,** 366 (1924); 6.
Stewart and Morrow, Phys. Rev. **20,** 232 (1927); 1, 2.
Katz, Zeits. f. Physik **45,** 97 (1927); 1, 2, 5, 7.
Sogani and Raman, Nature, Apr. 23, 1927; 5.
Sogani, Ind. J. of Physics, **I,** 357 (1927); 5, 7, 10.
Sogani, Ind. J. of Physics, **II,** 97 (1927); 8.
Katz and Selman, Zeits. f. Physik **46,** (1928); 6.
Krishnamurti, Ind. of Physics **II,** 501 (1928); 10, 5, 7.
Stewart, Phys. Rev. **33,** 889 (1929); 3, 4, 5, 7.
Vaidyanathan, Ind. J. of Physics **III,** 391 (1929); 1.
Krishnamurti, Ind. J. of Physics **III,** 508 (1929); 9.
H. H. Meyer, Ann. d. Physik **5,** 701 (1930); 10.
Stewart, Phys. Rev. **37,** 9 (1931); 10.
Good, Helvitica Physica Acta **III,** 205 (1930); 10.
Tanaka and Tsuji, Kyoto Coll. Sci. Mem. **13,** 1 (1930); 1, 2, 5, 6, 8.

[4] Wyckoff, Am. J. of Sci. **5,** 455 (1923).

[5] Krishnamurti, Ind. J. Phys. **2,** 501 (1928); **3,** 209 (1928); **3,** 307 (1928); **3,** 331 (1929); **3,** 507 (1929).

Hertlein[6] reported halos for aqueous solutions of butyl, amyl, and heptyl alcohols and found in all cases a single major peak varying with composition and lying between the peaks of the components. This agrees with the experiments of Krishnamurti. Stewart's theory is used for explaining the results.

Good[7] has investigated the diffraction of x-rays by water and by aqueous solutions of certain electrolytes. He applies all of the theories which have been suggested to explain the diffraction and concludes that the existence of cybotactic groups affords the most satisfactory interpretation.

Tanako and Tsuji[8] photographed the halos of a number of organic solutions and found no disagreement with Krishnamurti but these authors state that the results were too indistinct to obtain any conclusive evidence.

Apparatus

The apparatus is the same as that used by Stewart and Morrow.[9] The specimens of liquid were contained in sealed cyclindrical thin walled soft glass capsules which were from 0.5 to 0.8 of the computed optimum thickness, except in the case of tetranitromethane. In this case the optimum thickness is so small that the cylindrical tube used would not intercept enough of the beam to produce scattered intensities capable of accurate measurements.

Mo$K\alpha$ radiation filtered through 0.35 mm of zirconium oxide was used for the diffraction. No measurement was made of the operating voltage since the dependable test for correct adjustment was the reduction of voltage until any significant effect of general radiation disappeared. At this voltage the general radiation peak occurred at approximately 6 A. The inverse voltage in the tube (transformer voltage without rectification was used) was roughly 30 kv.

Observations were made at intervals of 0.5° and the published curves are composites of three or more originals.

Results

The diffraction curves are given in Figs. 1, 2, and 3. Each figure represents a single mixture and each curve a different concentration. The ordinates are relative intensities and in each curve the highest point is given a value of 100 so that the relative intensities of different curves are not indicated. The ordinates of successive curves are displaced in order to compare the positions of the peaks.

The question arose as to the ability of the spectrometer to resolve the peaks of the constituent liquids if they were all present. A curve was obtained by placing a capsule of ethyl alcohol and one containing methylcyclohexane side by side in the spectrometer and the resulting diffraction plotted. The lowest curve of Fig. 2a is the result. This test indicated that when the two peaks are in the diffracted beam, the spectrometer can resolve them.

[6] Hertlein, Zeits. f. Physik **54,** 341 (1929).
[7] W. Good, Helvetica Physica Acta **3,** 205 (1930).
[8] Tanako and Tsuji, Kyoto Coll. Sci. Mem. **13,** 17 (1930).
[9] Stewart and Morrow, Phys. Rev. **30,** 232 (1927).

Figs. 1 and 2 are the diffraction curves for mixtures which evidently form a single type of cybotactic group, or mixtures to which the author would prefer to give ths specific term "solution." Fig. 2b shows the diffraction peaks of mixtures of phenol in water. The curves for 94.1, 83.0 and 70.0 percent phenol are emulsions at ordinary temperatures. These three specimens were heated by blowing a blast of heated air upon them and kept just warm enough

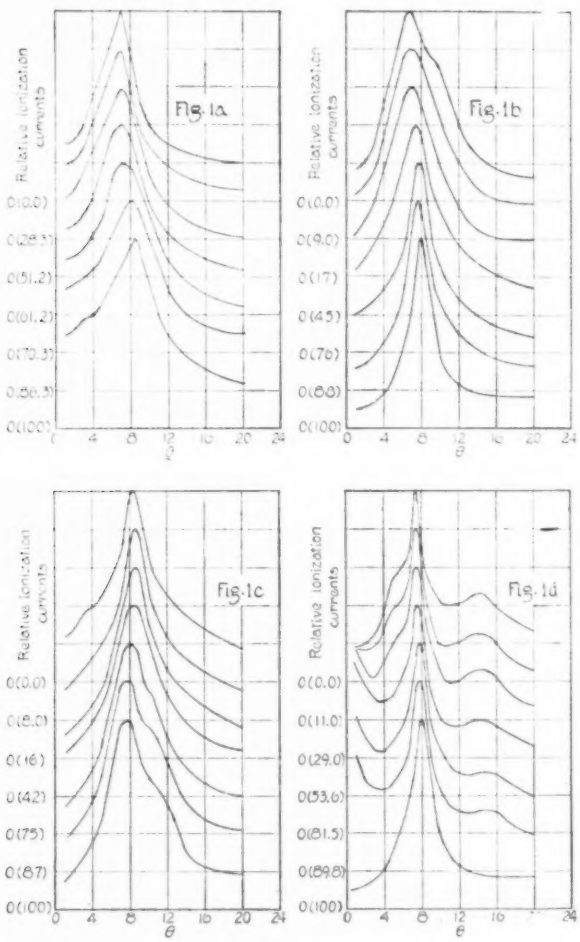

Fig. 1. Relative ionization curves for solutions. (a) N-butyl alcohol in o-dimethylcyclohexane; (b) Cyclohexane in paraldehyde; (c) Quinoline in phenol; (d) Cyclohexane in tetranitromethane.

to make them clear solutions. The lowest two of the curves were taken at 40°C and the uppermost of these three at 65°C. In Fig. 3 the curves in solid line represent the data for the three percentages specified above but at 27°C at which temperature they were milky emulsions. The data for the 98.2 and 57.9 percent phenol are shown in dotted line. They also were taken at 27°C and were clear solutions.

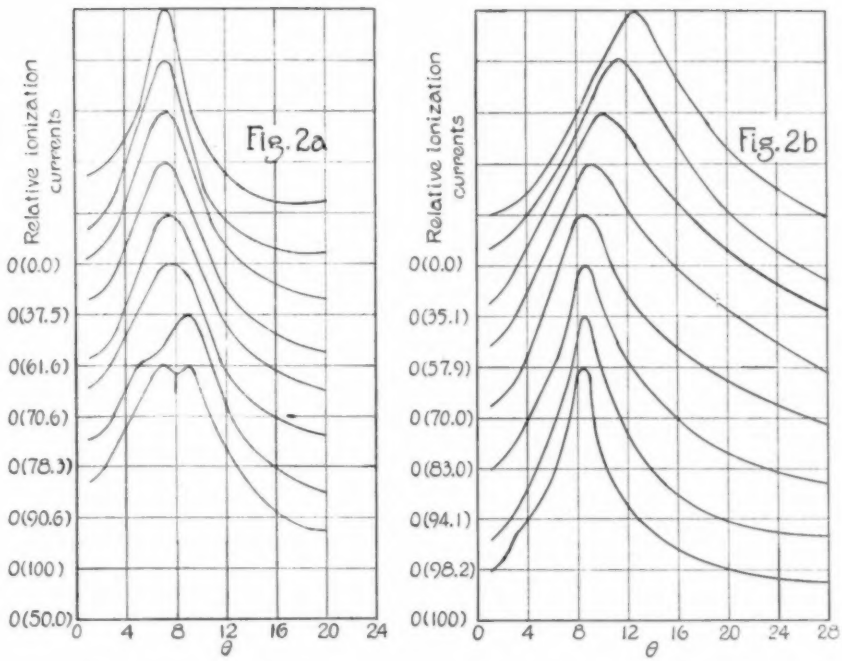

Fig. 2. Relative ionization curves for solutions. (a) N-ethyl alcohol in methylcyclohexane; (b) Phenol in water.

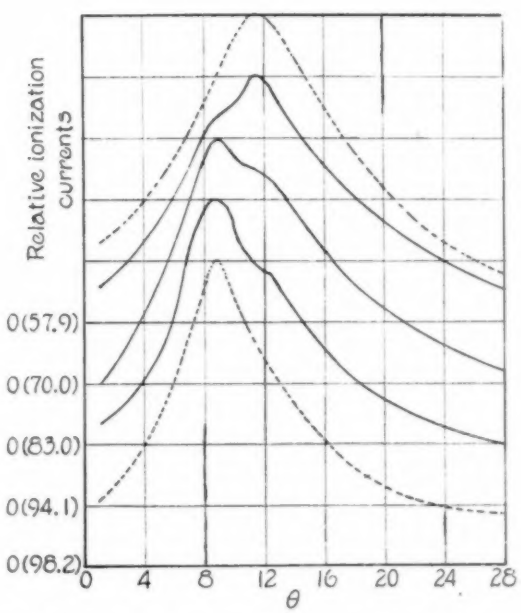

Fig. 3. Relative ionization curves of phenol in water compared with those of the constituent liquids.

Figs. 4, 5 and 6 were obtained by substituting in Bragg's law angles corresponding to the peak intensity values. There is thus obtained the most probable planar spacing or distance between planes of symmetry in the mole-

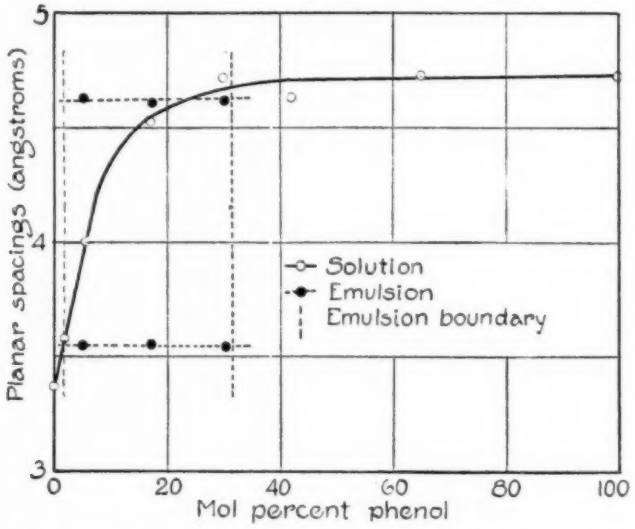

Fig. 4. Most probable spacing between planes in mixtures of phenol in water.

cular groups. Fig. 4 contains both the curves for the phenol-water solution in full line, and the two spacings for the emulsions in horizontal broken lines. The vertical broken lines represent the boundaries of the concentration range in which the mixture exists as an emulsion at room temperature.

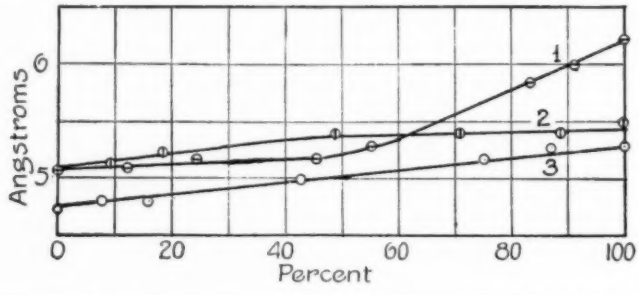

Fig. 5. Most probable spacing between planes in mixtures. (1) Paraldehyde in cyclohexane; (2) Tetranitromethane in cyclohexane; (3) Quinoline in phenol.

The planar spacings computed from the peak intensities of the pure liquids used are given in Table I. The curves for all the liquids have been described by Stewart and Morrow,[10] and Stewart,[11] with the exception of paraldehyde, quinoline and tetranitromethane. Paraldehyde and quinoline are ring compounds and their diffraction curves (Fig. 1b and 1c) with one major and one

[10] Stewart and Morrow, Phys. Rev. **30,** 232 (1927).
[11] Stewart, Phys. Rev. **33,** 889 (1929); Phys. Rev. **37,** 9 (1931).

minor peak are similar to those of certain ring compounds described by Stewart. The longer spacing is probably a molecular dimension and the smaller spacing is possibly a separation between planes which is less than a molecular dimension.

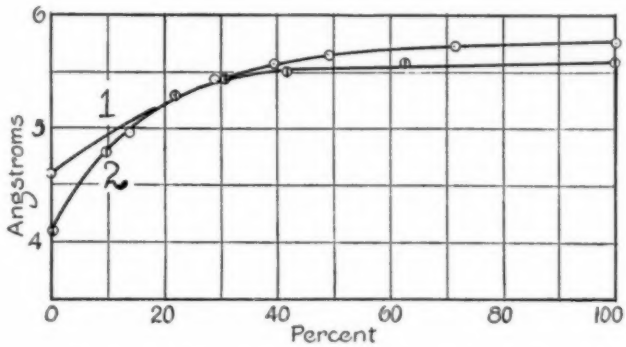

Fig. 6. Most probable spacing between planes in mixtures. (1) O-dimethylcyclohexane in n-butyl alcohol; (2) Methylcyclohexane in n-ethyl alcohol.

The diffraction curves of water (Fig. 2b) contain one very broad major peak. Stewart[12] and Meyer[13] have found secondary peaks at 18.8° and 31.1°. These peaks are quite prominent at low temperatures.

TABLE I. *Spacings between planes of symmetry.*

No.	Name	Spacing in A. u. a	a'
1.	N-ethyl alcohol	4.16	5.80
2.	N-butyl alcohol	4.78	8.47
3.	Methylcyclohexane	5.60	
4.	O-dimethylcyclohexane	5.70	
5.	Cyclohexane	5.05	
6.	Paraldehyde	6.20	3.90
7.	Phenol	4.75	11.60
8.	Quinoline	4.30	3.77
9.	Tetranitromethane	5.40 5.55*	
10.	Water	3.44	

* Obtained from second order peak.

The tetranitromethane is symmetrical in form being made up of four NO_2 groups around a carbon atom. The molecule is very heavy and produces strong diffraction and the symmetry should permit a more perfect lattice than do some of the other liquids. These points are borne out by the unusually sharp major peak (Fig. 1d) and by the persistence and intensity of the second order peak. There is a second minor peak shown in the figure at 5°, probably due to general radiation rather then to the 0.71A which produces the major peak. This occurs because the specimen exceeded the optimum thickness, the

[12] Stewart, Phys. Rev. **37,** 9 (1931).
[13] H. H. Meyer, Ann. d. Physik **5,** 701 (1930).

shorter wave-length of the general radiation scattering being more emphasized. A third interesting feature of the tetranitromethane curve is the large scattering at very small angles. This scattering at small angles is more pronounced in the solutions. Krishnamurti[14] agrees in the main peak and scattering at small angles, but, because of a lower voltage does not have the peak here attributed to general radiation.

Discussion

The general statement of results regarding mixtures may be itemized as follows:

(a) *Nonemulsions.*

(1) The nonemulsions in every case exhibit a common major diffraction peak.

(2) This peak shifts continuously in the direction of the major peak of that constituent, the concentration of which is increasing.

(3) The major peaks of nonemulsions are in general somewhat broader than those of the pure liquids.

(4) Minor or secondary peaks are found in some of the nonemulsions when there are secondary peaks in one of the constituents. These secondary peaks (belonging to the solvent) shift and disappear as the concentration changes.

(b) *Emulsion.*

(5) The emulsion contains two major peaks.

(6) These peaks remain constant in angular position being identical with those of the pure liquids involved.

(7) The relative intensity of the two peaks is apparently directly proportional to the molecular concentrations of liquids to which they correspond.

The existence of a single peak in a solution when the constituents if separate produce two peaks, indicates a single type of moleculer grouping rather than two types. The variation of the position of this peak with the concentration along a smooth curve as in Figs. 4, 5 and 6, terminating in the spacing values for the pure liquids indicates that this single molecular grouping is formed of molecules of both constituents.

The slight widening of the curves for solutions compared with those for pure liquids suggests less sharpness of variation of the probability values of the distance between planes, compared to that of the pure liquid. In a concentrated solution the presence of molecules of the solute modifies the important planes of symmetry causing the shift in the major peak and modifies and finally obliterates those less important planes of symmetry which produce the secondary peak, thus shifting and finally causing the disappearance of the secondary peak. The above conclusions lead to the description of a solution as a mixture containing cybotactic groups into which enter molecules of both constituent liquids.

[14] Krishnamurti, Ind. J. of Physics **3**, 508 (1929).

This conclusion is analogous to that obtained in the x-ray analysis of certain solid solutions or alloys of metals.[15] In the case of alloys there are two classes. In the first, the two pure metals have the same crystal form, and in the second, they have different crystal forms. But in both cases the alloy has a single crystal form at a given concentration and both kinds of molecules enter this single type of crystal. In the second case the crystal form changes from that of the first metal to that of the second at some definite concentration. While this very important similarity of mutual participation in the groups exist between solid and liquid solutions yet there is a very marked difference between solid crystals and liquid cybotactic groups. In the solid, the groups are very regular, permanent, quite homogeneous and definite in form. In a liquid the groups are semiorderly, and more or less temporary. At any instant they are densely distributed throughout the liquid with their vague boundaries shaded off from one to another surrounded by less organized molecules. Within the groups the arrangement is not as perfect as in the crystal, since the separation of planes is a matter of probability.

The existence in the diffraction of the emulsion of two peaks which are identical in position with the peaks produced by the constituent liquids indicates that there are two different types of cybotactic groups in the mixture and that the groups are the same as those of the constituent liquids. The fact that the relative intensity is proportional to the concentration is due to the relative number of each type of group present in the mixture.

In Fig. 6 the ordinates of the two horizontal broken lines are the most probable spacings for the liquids which make up the emulsion. These spacings correspond not to those of phenol and water but to the saturate solutions of phenol in water and water in phenol, the concentrations of which are shown by the vertical lines. This is exactly what should be expected from the hygroscopic property of phenol and the partial miscibility of phenol and water.

In general, the results reported in this paper and the conclusions drawn from them agree with those of other writers. However, it is desirable and necessary to make clear the differences in conclusions between the contribution of Krishnamurti[16] and the author. They are, first, the classification of mixtures, second, the x-ray diffraction differences found in his classifications, and third, the scattering near zero angle. As to the first and second, it may be said that Krishnamurti's classification cannot be correlated with the x-ray diffraction results. His classification is based upon the ability of a separation of the components of the mixture by the addition of sodium chloride. In the first class are those inseparable mixtures and in the second, separable mixtures. But there are miscible mixtures in both classes which according to Krishnamurti give similar x-ray diffraction. The author's simple classification into miscible and nonmiscible mixtures is in agreement with x-ray results. That is sufficient reason for adopting the author's classification in the present discussion. In regard to the differences in x-ray diffraction effects, they are limited to the cases of phenol-water, trimethyl carbinol, water, and piper-

[15] Wyckoff, Structure of Crystals, Chem. Cat. Co. (1924).

[16] Krishnamurti, Ind. J. of Physics **3**, 331 (1929).

idine-water mixtures. In the former, the author's experiments and the results in Fig. 6 would seem to take precedence over those of Krishnamurti who does not state whether the mixture is an emulsion or not. Indeed there is agreement if it is assumed that Krishnamurti's observations are taken at room temperature. There then remain the cases of trimethyl carbinol-water, and piperidine-water mixtures, and the difference in scattering at an angle near 0°. The author was unable to secure samples of the above liquids and was thus compelled to forego any check on Krishnamurti's results. The printed copies of his photographs do not clearly indicate the second peak claimed. The last difference in the scattering near 0° is a minor one, having little or no bearing upon the general conclusions of the present paper. It can therefore be said that Krishnamurti and the author, with the possible exceptions of trimethyl alcohol-water and peperidine-water, agree that a binary mixture wherein the two liquids are miscible, will give a single major diffraction instead of the individual peaks of the component liquids. Indeed, with the possible exception mentioned above, and the early observations of Wyckoff,[15] there is now agreement in the concept of the formation of a single type of cybotactic group if the liquids are miscible.

With regard to scattering at small angles there is also a minor disagreement between Krishnamurti and the author. The former states that in very weak solutions the solute particles do not take part in any formal arrangement but have a random distribution and scatter similarly to a gas, thus producing large diffraction at small angles. In high concentrations these solute particle lose their chaotic distribution and take part in the organized groups which produce coherent scattering. It is generally known that all pure liquids produce quite an appreciable amount of scattering at small angles and the results of this paper show scattering at small angles for all solutions regardless of concentrations and no case of decrease in scattering with increase in concentration. In fact there is the one case of tetranitromethane (Fig. 1d) in which the pure liquids is unusually low in this scattering at small angles but shows an unusually large amount at high concentrations of a solution in cyclohexane. If the solute did not enter the groups producing the peaks there would be no shift in the peak, which is contrary to the results reported here. It is to be understood that the cybotactic condition in a liquid does not assume that at any instant every molecule is involved in a group. There are many molecules present which are not at that instant in any group. A condition exists somewhat to that existing at the surface of an enclosed liquid where molecules are continually leaving and entering the liquid. Molecules are continually leaving and entering the groups. These migrating molecules have a random distribution and produce the scattering at small angles. In the solution, due to the lack of homogeneity, the number of molecules having this random distribution is probably greater than in the pure liquids, thus producing greater scattering at small angles. The fact that solutions of tetranitromethane have exceptionally large scattering of this type is probably due to an additional cause. This liquid is quite unstable and may break down to some extent and the decomposition products containing heavy atoms would produce an unusually large scattering.

It is generally accepted that the definition of a solution is a mixture existing in a single phase. It may also be defined as a mixture the components of which cannot be separated by mechanical means. A definition involving the actual internal distribution could not be found by the present author. The common criteria of a liquid solution according to Jones[17] are osmotic pressure, lowering of freezing point, and raising of the boiling point. Raoult stated certain quantitative laws concerning the freezing and boiling points from which all solutions deviate. It is the obvious conclusion of the results of this paper that a solution may advisedly be regarded as a mixture of pure substances in which there is a single type of cybotactic group in which the molecules of both kinds participate.

There are a number of classes of nonsolutions such as emulsions, gels, colloids and sols. The size of the aggregates vary. The ultimate emulsion would be a mixture of single molecules. This ultimate emulsion has been suggested as the internal picture of a solution, but the radical difference in the behaviour of solutions and emulsions indicates that there is a greater difference than simply the size of the aggregate. It is now suggested that this difference in behaviour of solutions and emulsions is due to the presence of the cybotactic groups. The apparent homogeneity of a solution may be in the homogeneity of the groups. The change in the groups of the solvent due to the presence of solute molecules is regarded as the cause of the change in boiling and freezing points. The energy relations of the groups, producing a "tendency" to form them may be the description of the origin of osmotic pressure.

The association of molecules into aggregates or large complex multiples of single molecules has been inferred from the fact that the molecular weight determined from physical properties is in certain cases greater than those determined by chemical methods. The degree of association is defined as the ratio of apparent molecular weight to the true chemically determined weight. Longinescu[18] points out that this degree of association in a large number of organic liquids is proportional to the number of molecules per unit volume. He suggests that these physical properties from which association is inferred, are influenced by this variation in the number of simple molecules in a unit volume rather than the so-called complexity of the molecules. It is obvious that the cybotactic group condition is an adequate description of association and has, in addition, a direct proof of its existence through x-ray diffraction.

The author wishes to express his most sincere appreciation to the members of the faculty of the Physics Department of the State University of Iowa for their assistance and suggestions, and in particular to Professor G. W. Stewart who proposed the problem and under whose direction the work was done.

[17] Jones, Nature of Solutions, Van Nostrand, (1917).
[18] Longinescu, Chem. Rev. **6**, 381 (1929).

DEPENDENCE OF COMPTON LINE BREADTH ON PRIMARY WAVE-LENGTH WITH THE MULTI-CRYSTAL SPECTROGRAPH

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Abstract

The present report is a continuation of the work reported previously. The main purpose of the research is to test the correctness of the assumption that the initial velocities of electrons in the scattering body cause the observed breadth of the Compton shifted line. In the previous paper the natural breadths of the Compton line were observed for different angles of scattering and the breadth was found to obey the functional dependence on scattering angle predicted by DuMond on the assumption that electron velocities cause the breadth. According to DuMond's theory the breadth should also be nearly proportional to the primary wave-length. This point is tested in the present paper. Exposures of about one thousand hours each were made with characteristic K radiation from molybdenum, silver and tungsten target tubes. In each case the radiation was scattered from a graphite scatterer at a very well defined large scattering angle of 156°, the multicrystal spectrograph being used to analyze the scattered radiation. Reproductions of the photographic spectrograms are shown and also microphotometer curves of the spectra. The breadth of the Compton line is found to diminish with shorter primary wave-lengths in complete accord with the predictions of DuMond's theory. Unless some other cause can be found to explain the observed behavior of the breadth the results of this paper and the above mentioned previous paper constitute a complete vindication of this theory and of its basic assumption that the initial velocities of the electrons in the scatterer cause the breadth of the Compton shifted line. If this is correct, then these experiments constitute direct experimental evidence of the dynamic nature of atoms. The Compton shifted line can indeed be thought of as broadened by the Doppler effect of the motion of the scattering electrons. A simplified form of the theory of modified scattering by initially moving electrons is presented to supplement and clarify the more elaborate and exact theory of the previous paper. We call attention to the fact that the theory and experimental results are in no way discordant with wave mechanics or the uncertainty principle but we believe that to translate the present exposition into the language of wave mechanics would tend to obscure rather than clarify the picture. The results of this work are so clearly defined that the reality of the much narrower Compton lines obtained recently by several investigators seems, in our opinion, to be very doubtful.

Purpose of the Investigation

IN A recently published paper[1] the authors have described a study undertaken to test whether the initial velocities of electrons in a solid body of low atomic number scattering x-rays cause the observed broadening of the Compton shifted line. A theory based on the assumption under test was presented in that paper which predicted the behavior of the breadth of the shifted line as a function of the scattering angle and primary wave-length. If $\Delta\lambda_{1/2}$ is the breadth at say half maximum value then it appeared from this theory that

$$\Delta\lambda_{1/2} = 4\beta_{1/2}\lambda^* \tag{1}$$

[1] DuMond and Kirkpatrick, Phys. Rev. **37**, 136 (1931).

when $\beta_{1/2}$ = the speed of that class of electrons in the scattering body possessing the velocities which cause the broadening at half maximum value and where

$$\lambda^* = \tfrac{1}{2}(\lambda_1^2 + \lambda_c^2 - 2\lambda_1\lambda_c \cos\theta)^{1/2} \tag{2}$$

λ_1 = primary wave-length incident on the scatterer. $\lambda_c = \lambda_1 + (h/mc)(1 - \cos\theta)$ = Compton shifted wave-length for initially stationary electrons. θ = scattering angle.

If the Compton shift is small compared to the wave-length, that is, if λ_1 and λ_c differ by a very small amount relative to either one, then from (1) and (2) it is evident that approximately

$$\Delta\lambda_{1/2} = 4\beta_{1/2}\lambda_1 \sin\tfrac{1}{2}\theta. \tag{3}$$

To a first approximation then the breadth of the Compton line should be proportional to the primary wave-length and to the sine of half the scattering angle if the breadth is to be regarded as an effect of electron velocities.

The paper above referred to reported the results of a test of the dependence of Compton line breadth on scattering angle. Long x-ray exposures on photographic spectrograms of molybdenum K radiation scattered from graphite at three different and very well-defined scattering angles were taken using the multicrystal spectrograph which permits of high spectral resolution and great homogeneity of scattering angle. The breadth of the Compton shifted line was shown by these experiments to obey very satisfactorily the predicted functional dependence on scattering angle. The results constituted only a qualitative test of the dependence of Compton line breadth on primary wave-length however because only two wave-lengths appeared on the spectra, namely $K\beta_1$ and $K\alpha_{12}$ differing by only about ten percent. A slight systematic difference in the breadth of the two corresponding lines did however appear in the right direction and roughly of the right magnitude.

The purpose of the present investigation is to test more thoroughly this dependence of Compton line breadth $\Delta\lambda$ on primary wave-length λ. The point is important because the postulated broadening of the Compton line by the velocities of the scattering electrons can be regarded as a Doppler broadening and the approximate constancy of $\Delta\lambda/\lambda$ is a very characteristic property of such a phenomenon.

The previous paper[1] above referred to contained an analytical solution of the problem of the modified scattering of x-rays by ensembles of moving electrons. This solution can be presented in a very vivid and simple form by introducing two simplifying approximations .Having solved the problem rigorously in the previous paper the authors feel that it is valuable now to present the simple approximate exposition in the interest of clearness.

Simplified Theory of Compton Line Breadth

Two simplifying approximations are made:

1. The change in wave-length due to scattering is a negligible part of the wave-length itself.
2. Relativity is neglected.

In Fig. 1 the x-axis is taken in the bisector of the supplement of the scattering angle θ. The vectors $h\nu_1/c$ and $h\nu_2/c$ representing respectively the momenta of the incident and scattered quanta of radiation are by approximation

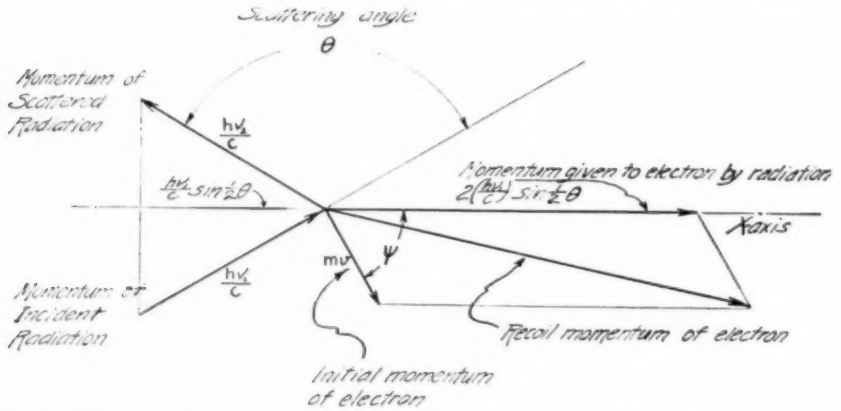

Fig. 1. Diagram of momentum vectors involved in the simplified approximate analysis of Compton scattering by an initially moving electron. The initial electron momentum is here much exaggerated relative to the momentum of the radiation. The plane of the angle ψ need not lie in the plane of the paper. Complete generality is obtained by rotating the plane of the angle ψ around the x-axis. This in no way affects the analysis here presented.

(1) nearly equal. Hence the change in momentum of the radiation, which is the momentum imparted to the electron, is given by

$$2\left(\frac{h\nu_1}{c}\right)\sin\tfrac{1}{2}\theta \tag{4}$$

and is directed along the x-axis.

The recoil momentum of the electron will be the vector sum of this acquired momentum and the initial momentum mv which the electron possesses at the instant of scattering in virtue of its natural motion in the atom or in the crystal lattice. The initial momentum mv may have any direction *in space* making an angle ψ with our x-axis. (In Fig. 1 the planes of the angles ψ and θ are shown both lying in the paper solely for convenience of drawing.)

$$(\text{Recoil momentum})^2 = (mv)^2 + 4\left(\frac{h\nu_1}{c}\right)^2\sin^2\tfrac{1}{2}\theta + 4(mv)\left(\frac{h\nu_1}{c}\right)\sin\tfrac{1}{2}\theta\cos\psi \tag{5}$$

The *recoil energy* is obtained by dividing this equation through by $2m$. Deducting from this result the initial energy $\frac{1}{2}mv^2$ possessed by the electron before scattering we obtain the energy abstracted by the electron from the radiation. Equating this to $h(\nu_1-\nu_2)$ we obtain

$$h(\nu_1-\nu_2) = \frac{2}{m}\left(\frac{h\nu_1}{c}\right)^2\sin^2\tfrac{1}{2}\theta + 2v\left(\frac{h\nu_1}{c}\right)\sin\tfrac{1}{2}\theta\cos\psi. \tag{6}$$

This is converted into wave-lengths by multiplying the last equation by $\lambda/h\nu$ and remembering from approximation (1) that $(\nu_1-\nu_2)/\nu_1=(\lambda_2-\lambda_1)/\lambda_1$. The change in wave-length due to scattering is

$$\lambda_2 - \lambda_1 = \frac{h}{mc}(1 - \cos\theta) + 2\frac{v}{c}\lambda \sin \tfrac{1}{2}\theta \cos\psi. \tag{7}$$

The first term represents the well known Compton shift, while the second term is the modification in the shift caused by the electron's initial velocity. Call this term, l. It may be quite appropriately regarded as a Doppler shift due to the component of the electron's motion along x. Since the electron may move in any direction, $\cos\psi$ can take all values between $+1$ and -1, and l can vary from $-2\beta\lambda \sin \frac{1}{2}\theta$ to $+2\beta\lambda \sin \frac{1}{2}\theta$. Thus the Compton line acquires a breadth

$$4\beta\lambda \sin \tfrac{1}{2}\theta \tag{8}$$

where $\beta = v/c$ for electrons moving in random directions and each having a speed v.

Consider the case of scattering by an ensemble of electrons, all having one and the same speed $\beta = v/c$ and randomly directed velocities. Let us inquire how the intensity will be distributed for such a case between the limits of the line breadth fixed by Eq. (8).

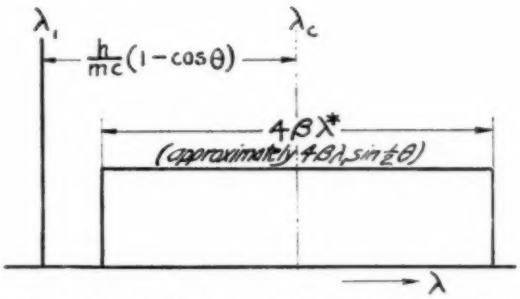

Fig. 2. Spectral energy distribution of modified scattered x-radiation for the ideal case of a monochromatic primary ray scattered by an assembly of electrons all of the same initial speed but with randomly orientated initial directions. The distribution is symmetrically disposed about the wave-length λ_c which is the shifted wave-length for initially stationary electrons. The distribution has a breadth $4\beta\lambda^*$ proportional to the speed of the electrons and is bounded by sharply defined discontinuities on both sides. Between these limits the distribution is uniform.

The chance of scattering by electrons directed so that their angles with the x-axis lie between ψ and $\psi + d\psi$ is:

$$P_\psi d\psi = \tfrac{1}{2} \sin\psi d\psi. \tag{9}$$

The shift away from the center of the Compton line for such electrons is:

$$l = 2\beta\lambda \sin \tfrac{1}{2}\theta \cos\psi \tag{10}$$

$$dl = -2\beta\lambda \sin \tfrac{1}{2}\theta \sin\psi d\psi. \tag{11}$$

Eliminating ψ and $d\psi$ between these equations, we obtain the chance that the shift shall lie between l and $l + dl$. It is:

$$P_l dl = (4\beta\lambda \sin \tfrac{1}{2}\theta)^{-1} dl. \tag{12}$$

The chance of scattering with a given shift l is thus independent of the shift between the limits:

$$-2\beta\lambda \sin \tfrac{1}{2}\theta < l < 2\beta\lambda \sin \tfrac{1}{2}\theta \tag{13}$$

and we conclude that the Compton line from an ensemble of randomly directed electrons, all of speed $\beta = v/c$ is a rectangular spectral distribution, as shown in Fig. 2.

In the real case the Compton line is doubtless due to scattering by electrons having not one speed β alone but a distribution over a considerable range of speeds. The spectral distribution must then be thought of as a superposition of such elementary rectangles of infinitesimal height and of breadth $4\beta\lambda \sin \tfrac{1}{2}\theta$ arranged one above another in decreasing order of breadth. See Fig. 3.

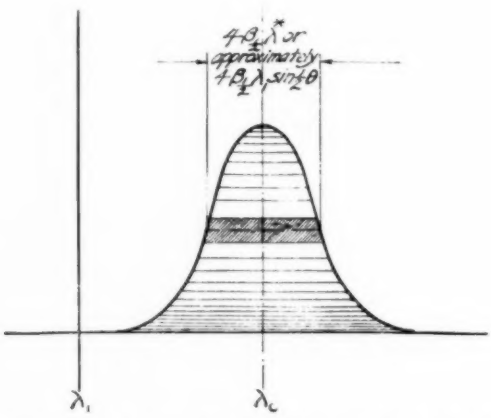

Fig. 3. Spectral energy distribution in Compton line for scattering of initially monochromatic x-radiation by an assembly of electrons distributed over a range of initial speeds and with random initial directions of motion. Each horizontal elementary rectangle is the contribution of the scattered radiation from one particular class of electrons of speed β in the range $d\beta$. The area of each rectangle is proportional to the relative electron population of its class. One of the rectangles will fall midway between the base and summit of the line and the speed corresponding to this class of electrons is designated by $\beta_{\frac{1}{2}}$.

The *area* of each such rectangle is to be made proportional to the electron population of the speed class β to $\beta+d\beta$ which the rectangle represents. Suppose we define the "breadth" of the line arbitrarily for convenience as the breadth at half maximum height and designate it by $\Delta\lambda_{1/2}$. Then

$$\Delta\lambda_{1/2} = 4\beta_{1/2}\lambda \sin \tfrac{1}{2}\theta \tag{14}$$

where $\beta_{1/2}$ is the velocity (referred to light) of the electron class that happens to fall in the line structure at half maximum height. This will remain the same class as we impose variations on θ and λ.[2]

[2] This statement is only true in a limited sense. The velocity $\beta_{\frac{1}{2}}$ will remain constant so long as θ is sufficiently large and λ sufficiently small to insure that practically all of the electrons in the scattering atom shall receive sufficient recoil energy to be set free from the atom in the scattering process. Unless this condition is fulfilled coherent (unmodified) scattering occurs.

We thus have arrived by very simple reasoning at an approximate expression for the behavior of Compton shifted line breadth as a function of scattering angle and primary wave-length. For the purpose of comparison with experimental observation we will use the slightly more accurate results of the

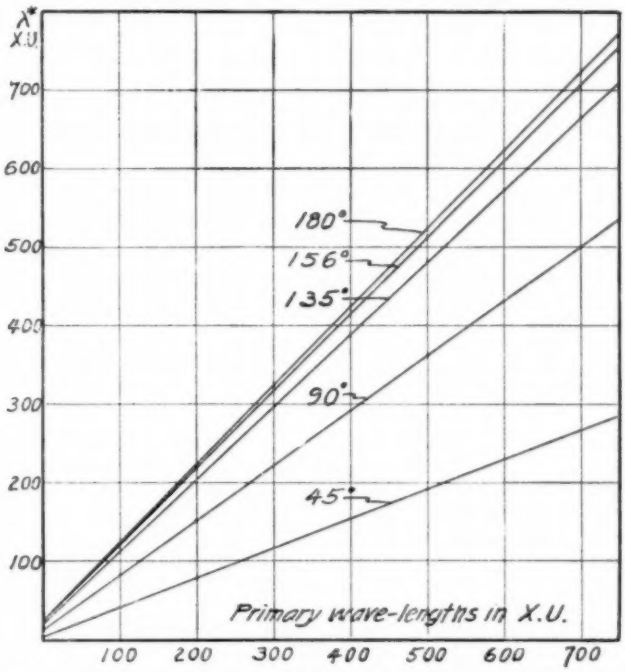

Fig. 4. Graphical representation of the dependence of Compton line breadth on primary wave-length for several scattering angles. The ordinates are values of λ^* which is proportional to the breadth provided $\beta_{\frac{1}{2}}$ remains constant. λ^* is about 35 times as great as the breadth at half maximum for the case of graphite.

exact analysis however. According to Eq. (14) the breadth of the Compton line in wave-length units should be proportional to the primary wave-length. The more exact analysis shows however that the breadth will not tend toward

Unmodified scattering probably occurs as follows: A free electron with specified initial momentum scattering radiation of wave-length λ under a specified angle will receive a definite recoil energy according to the laws of conservation of momentum and energy in the way shown by our theory. A bound electron having the same specified momentum will under the same specified conditions receive this same recoil energy if and only if this recoil energy exceeds the binding energy. If this recoil energy is less than the binding energy the electron will behave as though its mass were the mass of the entire atom and the laws of conservation of momentum and energy will then require an entirely negligible change in wave-length.

If an unmodified line appears this means, according to the above picture, that some of the electrons in the scattering atom part of the time are not contributing to modified scattering and these will on the whole be the more tightly bound electrons which are also the more swiftly moving electrons. There will thus be a slight selection in favor of slower electrons that will tend to reduce $\beta_{\frac{1}{2}}$ slightly when λ is sufficiently large or θ sufficiently small to make the unmodified intensity an appreciable fraction of the modified intensity. For the wave-lengths and scattering angles reported in this paper and the previous paper however we do not believe that such an effect plays any important part in the observed behavior of the shifted line breadth.

zero for very short wave-lengths. This can be seen from an examination of Eqs. (1) and (2). It is evident that as λ_1 tends toward zero λ^* does not vanish but tends toward the value $\frac{1}{2}(h/mc)$ $(1-\cos\theta)$ and the *Compton line for infinitely hard primary radiation* would still have a finite breadth given by

$$\lim_{\lambda\to 0} \Delta\lambda_{1/2} = 2\beta_{1/2}\frac{h}{mc}(1-\cos\theta). \tag{15}$$

Fig. 4 shows graphically the variation in the breadth of the Compton shifted line as a function of primary wave-length to be expected from the accurate theory. In order to get the ordinates in units independent of the factor $\beta_{1/2}$ which is of no interest in the present investigation, we have plotted in Fig. 4 the course of λ^* as a function of λ_1 for several scattering angles. (λ^* is about 35 times the breadth of the Compton line at half maximum value for the case of graphite.) The graphs of Fig. 4 are not quite straight lines. They may be represented analytically by the equation

$$\lambda^* = \lambda_1 \sin\tfrac{1}{2}\theta\left[1+\frac{k}{\lambda_1}+\frac{1}{4}\frac{k^2}{\lambda_1^2}\frac{1}{\sin^2\frac{1}{2}\theta}\right]^{1/2} \tag{16}$$

in which

$$k = 2\frac{h}{mc}\sin^2\tfrac{1}{2}\theta.$$

Experimental Test of Dependence of Compton Line Breadth on Primary Wave-length

The multicrystal spectrograph used in this work has been adequately described in previous articles[1,3] and will only be briefly referred to here. We have been delighted to find that in this instrument the fifty separate small Seemann wedge-type crystal spectrographs adjusted to exactly superpose their spectral lines on the negative have stayed in perfectly satisfactory adjustment for a period now exceeding one year. Reasonable care has been taken not to jar the table supporting the instrument. The feet of this table stand on large blocks of especially soft rubber.

Fig. 5 shows schematically the position of the x-ray tube, the graphite scatterer and the multicrystal spectrograph for the case of 156° scattering angle. All the work described in this article was done at or very near to this angle. In this position the tube is situated at a considerable distance from the scatterer, the greatest distance being 120 cm and the least distance 70 cm. This necessitates exposures of the order of one thousand hours but gives in return very fine homogeneity of the scattering angle. Under these conditions the spurious breadth of the Compton line due to inhomogeneity of scattering angle becomes utterly negligible.

The characteristic lines chosen to test the dependence of shifted line-breadth on wave-length were the K lines of molybdenum, silver and tungsten. General Electric water-cooled tubes were used for the molybdenum and

[3] DuMond and Kirkpatrick, Rev. of Scient. Inst. **1**, 88 (1930).

silver exposures, and a water-cooled glass Müller tube was used for the long exposure with tungsten. About half way through the tungsten exposure the Müller tube failed due to a temperature crack in the bulb. It was replaced by another tube exactly like it, great care being taken that the focal spot of the second tube should occupy exactly the same position as the focal spot of the first tube. The tubes ran continuously day and night. The molybdenum tube was held at 20 milliamperes and 50 kilovolts peak, the silver tube at 15 milliamperes and 73 kilovolts peak, and the tungsten tube at 10 milliamperes and 110 kilovolts peak.

An intensifying screen was used behind the film in the case of the exposure with tungsten tube. This is the only case with the multicrystal spectrograph in which we have used an intensifying screen. The screen has not been previously used in order to forestall the objection that our lines might be broadened by poor contact between the intensifying screen and the negative or

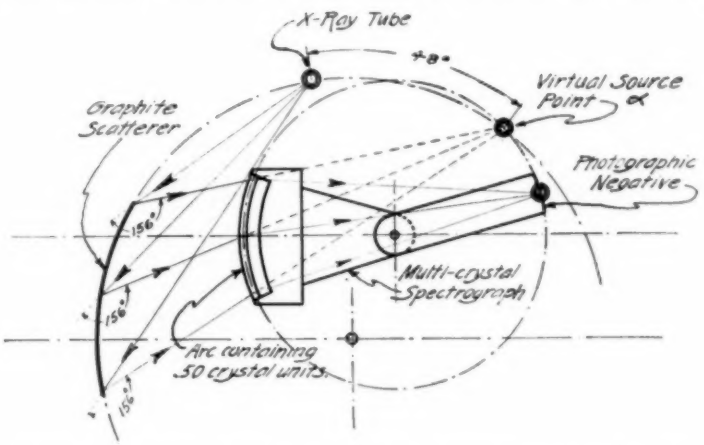

Fig. 5. Schematic diagram showing geometrical dispositions of x-ray tube, scattering body, and multicrystal spectrograph for 156° scattering angle. The setting for molybdenum radiation is the one here shown. For harder primary radiation the virtual source and spectral image are closer together.

that intensities might be falsified by the screen. Of the three exposures here reported the one with tungsten should, according to theory, and does in actual fact, have the narrowest shifted line breadth. It seems quite impossible for anyone to claim that the use of the intensifying screen could have rendered the line sharper or narrower. The sharpness of the primary reference lines appearing on the exposure with tungsten certainly leaves little doubt that the screen can be completely absolved of the suspicion of introducing any spurious effects.

The scatterer in all three cases consisted of a circular arc sawed from a large block of Acheson graphite. The focal spot of the x-ray tube and the arc of the scatterer were accurately located with respect to the point α of the multicrystal spectrograph by means of a plumb bob hanging from a radius arm exactly as described in the previous paper,[1] the focal spot being aligned with this plumb line by sighting from two mutually rectangular directions with

auxiliary plumb lines. The scattering angle could be measured with much better than the required accuracy by measuring the angle through which the radius arm must swing in passing from the point α of the multicrystal spectrograph to the focal spot of the x-ray tube. The exact values of the scattering angles for molybdenum, silver and tungsten were respectively 156°, $27' \pm 15'$, 155°, $21' \pm 15'$ and 154° $15' \pm 1°$ $30'$. The exposure times were respectively 897 hrs., 900 hrs. and 1020 hrs.

The bulk of the radiation from the silver and tungsten x-ray tubes was shielded by placing these tubes each in a housing consisting of a micarta tube wrapped on the outside with a sufficient number of layers of 1/16″ leaded rubber sheeting. The use of leaded rubber which combines the three properties of mechanical flexibility, opacity to x-rays, and good electrical insulation

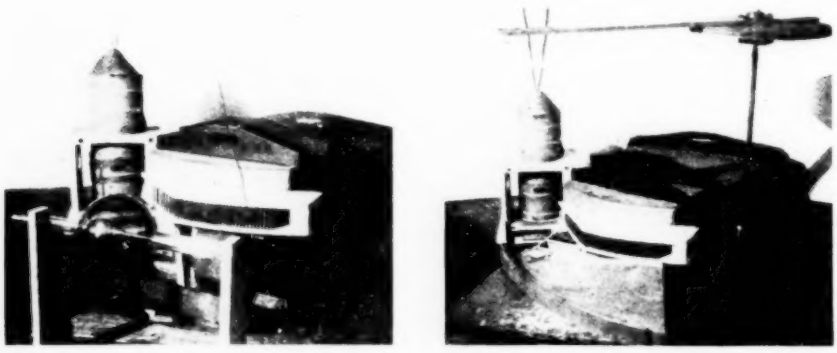

Fig. 6. Showing system of lead baffles used in the case of tungsten radiation. They are accurately located in front of the crystal arc of the multicrystal spectrograph. These baffles beside reducing the fogging due to amorphous scattering serve to shield the negative from strong radiation passing directly under the wedges without suffering reflection from the calcite faces. In the case of tungsten K radiation the reflexion angles are so small that this type of fogging becomes important. The right photograph shows the graphite scatterer in place for the long exposure with scattered radiation. The left photograph shows the scatterer removed and a tungsten x-ray tube situated on the swinging wooden sector for the short exposure to give the reference lines on the edge of the negative.

makes possible a much smaller, more compact and convenient tube housing than could be obtained with metallic lead, and eliminates the necessity for a bushing insulator. A hole was cut through the leaded rubber and micarta tube of just the right size and shape to permit an x-ray beam to illuminate the entire graphite scatterer. Another small hole was also cut at a point 90° around the cylinder from the above window to facilitate sighting the target with the plumb line.

The exposure with tungsten radiation required a considerable amount of preliminary work. The wedges in the crystal holders of the multicrystal spectrograph are of brass and have an angle of 120°. Tests were made, using direct radiation, with a sample unit to determine whether these brass wedges would be sufficiently opaque to the tungsten K radiation to give sharp, well-defined lines. They were found to be satisfactory.

The grazing angle with calcite for the tungsten $K\alpha$ lines is only about two degrees. The radiation which passes directly through under the wedge without reflection from the calcite has therefore a direction which differs from that of the $K\alpha$ lines by only two degrees. A system of fifty baffles of sheet lead 1/8″ thick was therefore designed and built with great care so that each baffle would cut off the straight-through radiation to one of the crystal units. The radiation coming from the scatterer in the proper direction to form the spectrum over the region of interest could however pass between the baffles. The alignment of the baffles was carefully checked by shining light from an incandescent bulb placed behind a paper slot situated on the film holder in the region of interest, the light passing backward to the crystals along the paths later to be followed by the x-rays (in reverse sense). The straight-through beams and the reflected beams from the crystals could be easily observed and the baffle holder could thus be adjusted so that the former were cut off and the latter permitted to pass. In Fig. 6 the lead baffles can be plainly seen.

It is a well-known fact that for a given scattering material and scattering angle the ratio of unmodified line intensity to modified line intensity diminishes with diminishing wave-length. For tungsten radiation scattered at large angles from graphite we did not expect to obtain any unmodified line at all and as a matter fact none appeared. Ordinarily the unmodified lines serve admirably the purpose of fiducial lines to establish the wave-length scale. In the case of tungsten the expected absence of the unmodified lines made it advisable to establish reference lines on the film. This was done by making an auxiliary exposure with primary tungsten radiation from a Coolidge tube placed in front of the spectrograph approximately in the position occupied by the scatterer which had been removed for the purpose. This exposure was made just after the 1020 hr. exposure with scattered radiation. A lead shield was introduced in front of the negative during this exposure with primary radiation so that only the edges of the negative were exposed. This was done to avoid all risk of fogging or falsifying the valuable 1020 hr. exposure. Of course great care was taken not to disturb the negative between the two exposures. The Coolidge tube used for this reference line exposure was gradually shifted by means of a screw so that it passed in front of a large number of crystals in the multicrystal spectrograph, thus giving a fair integration of the average position of the K lines from the crystals, rather than the position of these lines from one single crystal which might be very slightly displaced from the mean. In Fig. 6 the tube used for the reference line exposure can be seen standing on the swinging wooden sector which permitted moving it in front of the crystals.

Fig. 7 is a reproduction of the three negatives of molybdenum, silver and tungsten K radiation scattered from graphite. The decrease in Compton line breadth with decreasing primary wave-elngth is very clearly evident from an inspection of these reproductions. Attention is called to the sharpness of the unshifted lines and in the case of the tungsten exposure to the sharpness of the reference lines. These bear witness as to the good state of adjustment of the multicrystal spectrograph and preclude the possibility of the objection

being raised that the diffuseness of the shifted line might be caused by some instrumental defect. The narrowness of the Compton line in the case of the tungsten exposure is convincing evidence that the multicrystal spectrograph

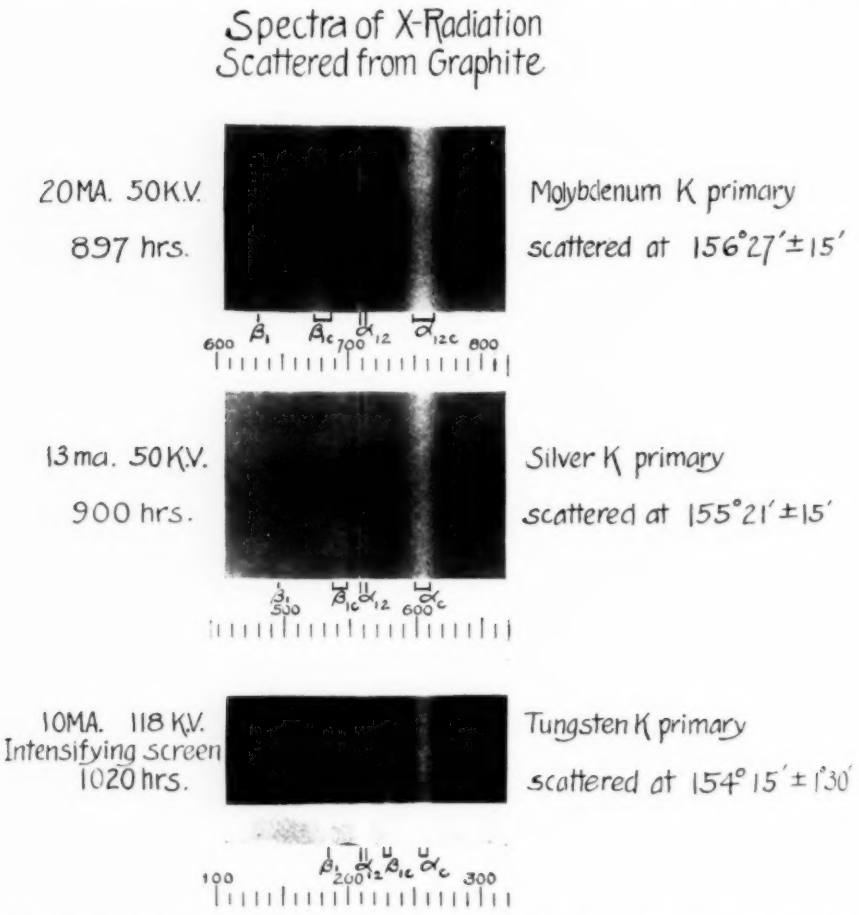

Fig. 7. Reproduction of three spectra of K radiation scattered by graphite at about 156°. The dispersion in wave-length units is the same on all three exposures as can be seen from the fact that the Compton shift for the $K\alpha$ lines is the same in all three cases. (At such a large scattering angle the slight variation in scattering angle between the three cases produces no detectable difference in shift.) Note the very evident diminution in the breadth of the shifted line measured in wave-length units as the primary wave-length diminishes. This is not an effect of over or under exposure or halation as the maximum density of blackening in the Compton line is very nearly the same in all three cases. A very considerable over exposure only very slightly broadens the narrow primary lines as can be seen in the case of the reference lines of tungsten. An intensifying screen was used in the case of tungsten only. These reproductions have been slightly intensified by the use of contrast printing paper to compensate for the loss in the half-tone process. A scale of wave-lengths in x-units accompanies each spectrum.

can give a narrow shifted line when such a narrow line is present. It satisfactorily eliminates the possible objection discussed in the previous paper[1] that our shifted line breadths might be exaggerated by multiple scattering or

by air scattering because there is no reason to expect such spurious scattering effects to be more pronounced for molybdenum or silver K radiation than

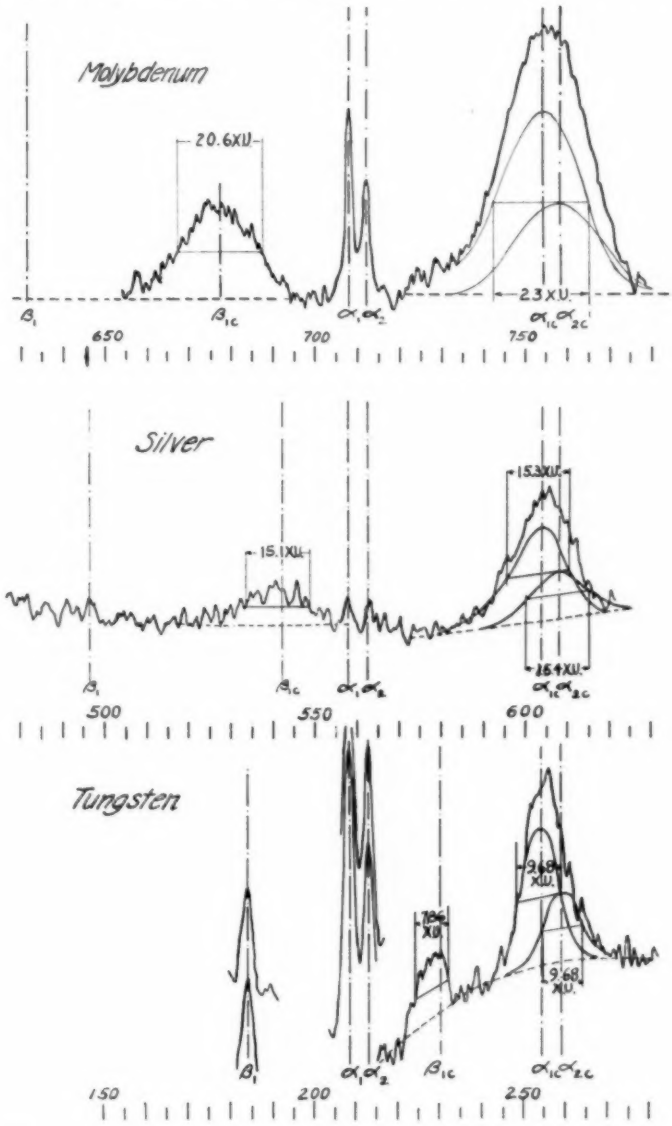

Fig. 8. Three typical microphotometer curves taken from the negatives shown in Fig. 7. A number of such curves were run on each negative in different regions of the height of the spectral lines. In the case of the tungsten spectrum the position of the reference lines had to be recorded by making two separate runs across the two edges of the film. This could be easily accomplished as the table carrying the negative on the microphotometer can be shifted laterally accurately normal to its direction of travel.

for tungsten K radiation. In fact, the evidence from the photographs shown in Fig. 7 seems to us to offer inescapable proof of the reality of the predicted and observed behavior of Compton line breadth.

In Fig. 8 typical microphotometer curves made from the above mentioned three negatives are shown. The shifted $K\alpha$ line is of course a superposition of two shifted lines corresponding to the two components of the primary $K\alpha$ doublet. The observed shifted $K\alpha$ line was graphically decomposed into its two components by the method already described in the previous paper.[1] This decomposition is a quite determinate process because of the fortunate fact that the relative intensity and wave-length separation of the two otherwise identical components is accurately known. In Fig. 8 the decomposed components are shown.

TABLE I. *Breadths in x-units* $\Delta\lambda_{\frac{1}{2}}$ *of shifted lines.*

Tungsten K rad.				Silver K rad.				Molybdenum K rad.		
Run	α_{1c}	α_{2c}	β_{1c}	Run	α_{1c}	α_{2c}	β_{1c}	Run	α_{1c}	β_{1c}
1	7.85	7.85	8.46	1	15.3	15.4	15.1	1	22.8	22.4
2	10.6	10.3	9.65	2	15.7	16.5	17.5	2	21.2	19.4
3	10.55	10.28	8.16	3	15.4	14.8	17.2	3	23.0	20.6
4	9.68	10.00	7.86	4	Bad	Blemish	16.0	4	23.0	20.6
5	9.68	9.68	7.86	5	15.9	14.8	15.1	5	21.9	21.5
				6	16.6	16.6	16.6			
				7	17.22	17.85	17.85			
Av.	9.67	9.62	8.39	Av.	16.02	15.99	16.48	Av.	22.4	20.9
	9.65		8.39		16.0		16.48		22.4	20.9

In Table I the breadths at half maximum of all the shifted lines are listed for all the microphotometer curves together with average breadths for the various wave-lengths. In Fig. 9 the individual and average breadths have been plotted as a function of primary wave-length for comparison with the theoretically predicted curve. Since the point to be tested is the functional dependence of breadth on primary wave-length and not the absolute value of the breadth one of the six observed breadths, namely the breadth of shifted Mo$K\alpha_1$ was arbitrarily fitted to the theoretically predicted curve, thus establishing the scale to which the other five observed breadths were plotted. The breadth variation checks the theoretical prediction to a precision well within the range to be expected.[4]

SIGNIFICANCE OF RESULTS

The two new physical effects whose prediction and observation we have reported in this paper and the previous one deserve a certain amount of critical discussion.

The quantitative fulfillment of the theoretically predicted behavior of Compton shifted line breadth is very clear and distinct. The simple and al-

[4] In Fig. 9 it will be noted that the observed breadths for the shifted tungsten lines fall slightly above the theoretical curve. If these were adjusted to fit the curve then the breadths for silver and molybdenum shifted radiation would fall below the curve. There is a bare possibility that this may in part at least be caused by the above mentioned decrease in $\beta_{\frac{1}{2}}$ by a selection in favor of slower electrons for the cases of softer radiation where unmodified scattering occurs. (See footnote 3) The relative faintness of the unmodified lines makes it appear much more likely however that the slight deviation (only about 2 X.U.) in the points for tungsten is merely an experimental error.

most classical nature of the theory so satisfactorily fulfilled must not however be interpreted as an indication that our results are in conflict with wave-mechanics. There is a tendency at present for physicists to feel suspicious of any theory not formulated in the language of the wave equation or of matrices, and a positive distrust is aroused if a theory becomes easy to visualize. The assumptions on which our theory of Compton shifted line breadth rests

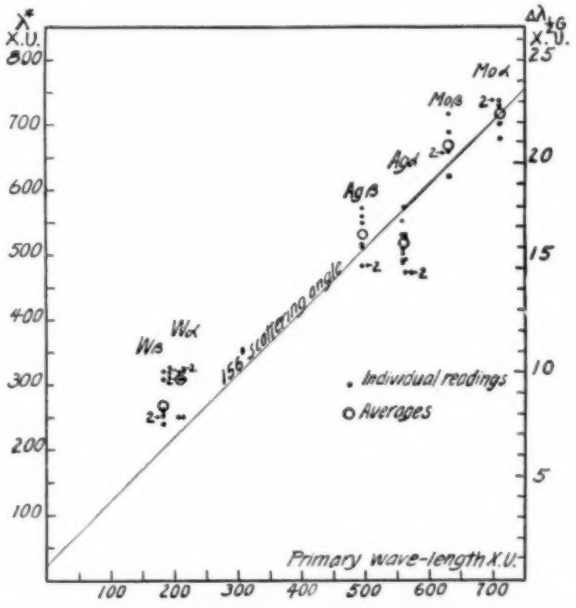

Fig. 9. Comparison of observed breadths of Compton lines for different primary wave-lengths with the theoretically predicted functional dependance of breadth on primary wave-length. The ordinate scale on the left is λ^* in X.U. The ordinate scale on the right is the breadth in x-units of the Compton line at half maximum value adjusted to fit the theoretical curve at one point only, namely the observed breadth of shifted Mo $K\alpha_{12}$.

are in complete accord with wave mechanics and do not in any way violate the Heisenberg principle of uncertainty. They are:

(1) and (2) Conservation of energy and momentum in individual processes.

(3) Probability of scattering by a given class of electrons (of speeds β to $\beta+d\beta$) proportional to the population of that class.

(4) Electron binding energy negligible compared to energy transferred to electron in scattering process.

(5) Initial electron velocity small compared to velocity of light.

It is clear that the uncertainty principle is not violated by our theory. The electron's *position* in our experiment is wholly undetermined and unspecified. Its velocity is therefore theoretically determinable with unlimited precision. This electron velocity can in fact be thought of as having been measured by observing the Doppler change in wave-length which it causes in the radiation scattered by the electron. Heisenberg discusses this very method of measuring the velocity or momentum of an electron in his book "The Physi-

cal Principles of the Quantum Theory" (page 25). *The broadening of the Compton line may therefore quite legitimately be thought of as a Doppler broadening caused by the initial velocities of all the electrons in the scattering body responsible for x-ray scattering.* (In the case of tungsten radiation scattered at large angles from graphite there seems to be little doubt that this means all six of the electrons in the carbon atom.)

An analysis of the structure of the broadened Compton line furnishes information as to the probability distribution of electron momenta in atoms. Indeed the *momentum eigenfunktion* of any atom can now be investigated by our method as readily as the *position eigenfunktions* have been determined in diffraction experiments. Analyses of Compton line structures into momentum eigenfunktions are soon to be published. Preliminary work of this kind indicates that the line structures so far obtained yield momentum eigenfunktions in good accord with the predictions of modern quantum mechanics.

It seems fair therefore to say that the broadening of the Compton line and the behavior of its breadth as a function of scattering angle and primary wavelength furnishes us with a direct experimental proof of the dynamic nature of the structure of atoms and solid bodies. The astounding electron velocities postulated by Bohr in his atom model which are still present with but slight modification in the quantum mechanics under the more sophisticated name of "momentum eigenfunktions" may be said at last to have been experimentally observed in about as real a sense as anything else in Physics can be observed.

The results of this work are so clearly defined that the reality of the much narrower Compton lines obtained recently by several investigators seems in our opinion to be very doubtful. This raises an interesting point in connection with determinations of the constant h/mc by measurements of Compton shift. It is evident that the smallest percentage error in the measured values will occur when the ratio of Compton line breadth to Compton shift is a minimum. The laws expressed in Eqs. (1), (2) and (3) show that the best conditions for measurement of h/mc occur at very short primary wave-lengths and large scattering angles. These conditions are fairly well satisfied by our exposure with tungsten radiations scattered by graphite at 156°. Precise measurements of shift from this exposure and others will be made the subject of a paper to be published in the near future. In our opinion the breadth of the Compton line even for these optimum conditions is too great to warrant an accuracy much better than one half percent in the determinations of h/mc and we fear that higher accuracy than this claimed by other investigators on the basis of apparently very narrow Compton lines has been illusory.

Further work with the multicrystal spectrograph will consist of an exploration of Compton line breadths and structures for various scattering materials.

In conclusion we wish to express our deep appreciation of the facilities put at our disposal by the Norman Bridge Laboratory and of the interest and encouragement given us by Dr. R. A. Millikan. This investigation which has involved a great deal of expense has been carried out with the aid of the Seeley W. Mudd X-Ray Research Fund. We take this opportunity to express our gratitude for this financial aid.

MOLECULAR ENERGY LEVELS AND VALENCE BONDS

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Abstract

Electronic energy levels in molecules are discussed, by the same methods previously used in discussing atomic levels. The problem in general is much more difficult than for atoms, and less progress can be made toward quantitative solution. For the lowest electronic level in cases where there are definite valence bonds, however, approximate solutions can be set up which should be fairly accurate, and which lead to a definite verification of the ideas of the writer and of Pauling regarding directed valence and the importance of concentrated bond functions. A number of special cases are discussed, involving both spin and orbital degeneracy.

THE writer has described in a previous paper[1] a method of discussing the structure of atoms according to wave mechanics. The purpose of the present paper is to extend similar methods to a consideration of electronic levels in molecules, particularly the lowest levels, resulting in molecular binding, giving first a general discussion and then some applications to specific cases. The molecular problem is in general much more difficult than the atomic one, and the definite results which can be obtained are far fewer. Nevertheless we can obtain some general properties of polyatomic molecules, in particular the directional properties of the valence bonds, which have already been qualitatively discussed by the present writer, and independently by Pauling.[2] In this connection we should mention recent papers by Heitler and Rumer and Weyl,[3] also discussing the quantum theory of valence bonds. These discussions are in one important respect more specialized than that of the present paper: they assume that the energy involved in molecular binding is small compared with that involved in the atomic multiplet structure in the atoms which compose the molecule, so that they can neglect all but the lowest atomic levels in discussing the molecular formation. This assumption is hardly justified in actual cases; and, more important, the characteristic directional properties which we have emphasized do not appear in this approximation at all, as Heitler and Rumer find, and as we shall show in a later section. Thus we cannot regard the treatment of Heitler and Rumer as being sufficiently general to be of very great physical significance, although in some special cases it is no doubt of value.

The first part of the discussion, in sections 1 to 4, deals with the general

[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[2] J. C. Slater, Phys. Rev. **37**, 481 (1931); Linus Pauling, Journ. Am. Chem. Soc. **53**, 1367 (1931).

[3] W. Heitler and G. Rumer, Zeits. f. Physik, H. Weyl, Göttinger Nachr., 285 (1930), 33 (1931).

description of the method, and is essentially similar to the method of dealing with atoms already described in the previous paper. In section 5 we take up a variety of special cases, developing most of the characteristic features in which the treatment of molecules differs from that of atoms by means of these illustrations. Section 6 summarizes these features, and sketches a general method for treating the lowest electronic levels of molecules in which the valence binding is of a conventional sort.

This paper was written while the writer was spending the summer at the University of California. He wishes to express his appreciation of valuable discussion with various persons there, particularly Dr. Henry Eyring.

(1) The Perturbation Theory

In the perturbation theory, it is assumed that we are given initially a set of functions u_i^0, forming in some way approximations to the real solutions of the problem. Then we try to set up linear combinations of these functions, $u_i = \Sigma(k) S_{ik} u_k^0$, which form much better approximations to the solutions. If H is the Hamiltonian operator of the problem, W_i the energy value associated with this function u_i, then Schrödinger's equation $Hu_i = W_i u_i$ becomes $\Sigma(k) S_{ik} H u_k^0 = W_i \Sigma(k) S_{ik} u_k^0$. Multiplying by u_j^{0*} and integrating, we have

$$\sum(k)(H_{jk} - W_i d_{jk}) S_{ik} = 0,$$

where $H_{jk} = \int u_j^{0*} H u_k^0 \, dv$, $d_{jk} = \int u_j^{0*} u_k^0 \, dv$. These form a set of simultaneous linear equations for the S's, which in general have no nonvanishing solutions unless the determinant of coefficients $(H_{jk} - W_i d_{jk})$ vanishes. Setting this equal to zero gives an algebraic equation for the energy levels W_i, and from the resulting values we can write and solve the equations for the S's. If the set of u_i^0's formed a complete set of functions, and if the linear equations and secular equation were rigorously solved, the resulting energy values and wave functions would be exact. But actually we are always driven to use some form of approximation.

First, the conventional perturbation theory commences by assuming that each unperturbed function u_i^0 is very nearly equal to the correct function u_i. Then H_{jk} is very nearly a diagonal matrix, whose diagonal terms H_{ii} are very nearly equal to the correct energy values W_i, and S_{ik} is very nearly diagonal, the diagonal elements being nearly unity. Thus we can make a power series expansion in terms of these various small quantities, with confidence that the series will converge. The familiar perturbations of first order, second order, etc., come from the successive terms of this expansion. Although this method is treated in most discussions as if it were the standard method of perturbations, there are as a matter of fact very few cases where it can be applied.

Instead, we generally meet the problem of degeneracy. Suppose that, in the absence of some perturbation, a number of stationary states have the same energy. Then any linear combination of their wave functions forms a correct wave function associated with that energy. In general, the particular combinations which we happen to have depend on convenience in setting them up. Now if the perturbation is applied, and the energy levels split up,

we no longer have this freedom of making linear combinations. The wave functions which are solutions of the unperturbed problem may be chosen as the u^0's, but then in general we shall not have one correct function u_i nearly equal to a corresponding unperturbed one u_i^0. Rather we shall have one correct one nearly equal to a certain linear combination of a set of unperturbed ones connected with the same unperturbed energy level. Thus we shall no longer have all nondiagonal matrix components of H nearly zero, and we cannot directly use the power series method. But it may happen that we choose our unperturbed functions in just such a way that these nondiagonal terms are zero anyway, and that we can expand in series after all. The perturbation method as applied to degenerate systems accomplishes just this. Its first step is to set up a so-called "zero order approximation." It does this by considering separately the small square parts of the matrix H_{jk} associated with states grouped together into a single degenerate set. By suitable linear transformations we can set up an intermediate set of functions u_i', such that just these nondiagonal components of the energy vanish. For a single square, the equations for the transformation are just like those written above for the general case, except that the indices run only over the finite set of degenerate states. Thus, at least sometimes, the problem is simple enough so that we can solve for the zero order functions u_i'. Next we can apply the regular perturbation theory, seeking a second transformation to the correct functions u_i, and solving by the power series method.

In actual problems in atomic and molecular structure, the method of formulating the perturbation problem which seems most suitable is based on the conventional method for degenerate systems, rather than on the power series method. The essence of the scheme is that we take a finite set of unperturbed functions, set up the finite secular equation and transformation coefficients, and so solve for a finite number of almost correct functions and energy level. Thus, having only finite things to work with, we have a real chance of obtaining exact solutions. Yet instead of taking together merely those few states associated with a really degenerate group of levels, we enlarge this group when feasible, to include all the neighboring levels which influence each other in an important way. At least in principle, we can imagine that we would add to our accuracy by considering more and more levels in our secular equation, approaching in the limit the exact solution, as mentioned in a previous paragraph. The conventional description of zero order, first order, and so on, of perturbation, is not applicable in this case. By analogy with the method used for degenerate systems, we have merely a zero order approximation. Yet actually our accuracy in most cases will be better than that of the first or second order approximations of the other methods, since as far as neighboring levels are concerned, we have what might be called infinite order approximations.

Our method, then, is this. We take a finite set of functions u_k^0, $k = 1 \cdots n$, and set up an equal number of linear combinations of them, $u_i = \Sigma(k = 1 \cdots n) S_{ik} u_k^0$, where the S's are determined by

$$\sum(k = 1 \cdots n)(H_{jk} - W_i d_{jk}) S_{ik} = 0, \; i, j = 1 \cdots n,$$

and where the energy levels W_i are the roots of the nth degree secular equation formed by setting the determinant of coefficients equal to zero.

One interesting observation relating to the method is the following: we may regard u_i as being a function containing the n parameters S_{ik}, $k=1 \cdots n$. If then we apply the variation method to our problem, stating that that function is the nearest to a solution of Schrödinger's equation which makes the mean energy $\int u_i^* H u_i \, dv$ stationary with respect to variation of the parameters, keeping $\int u_i^* u_i \, dv$ always equal to unity, then a simple application of the method of undetermined multipliers leads to equations for the S's, which are identical with the linear equations obtained above from the perturbation. method. Thus our procedure can be equally well considered as a method of perturbations or of variations.

Having stated our method of perturbations, we may now proceed to the problem. There are three important parts to it, forming the subjects of the three following sections: first, setting up the unperturbed functions; second, setting up the matrix components of energy and unity with respect to these functions: third, solving the secular equation and equations for the S's.

(2) Unperturbed Wave Functions

The unperturbed wave functions u_i^0 from which we start are all functions of coordinates and spin, antisymmetric in the electrons. We build them up, for molecules as for atoms, from combinations of one-electron wave functions. In this we differ from the other writers, as Heitler and Rumer, who have worked in this field, for they assume the atomic problem already solved, and build up molecular functions out of atomic functions rather than electronic ones. There seem, however, to be essential advantages in the present method, which have been missed by the other writers.

Suppose there are N electrons in our system, whether it be an atom or a molecule. Then to set up a single unperturbed function, we assign a single set of quantum numbers, or one-electron wave functions, to the electrons. For example, let us suppose that one has the wave function A, another the function B, etc., up to a final function E, say. Each of these is a function of three coordinates of position, and one of spin, of a sort which we discuss later. Let the coordinates (of position and spin) of the first electron be denoted by 1, of the second by 2, etc. Then we could set up an approximate function as the product

$$A(1)B(2) \cdots E(N).$$

But this would not be antisymmetric in the electrons, and to set up such a function, we add together all $N!$ functions formed by making all possible permutations of the functions $A \cdots E$ (which by the exclusion principle must be all different), each with a coefficient $\pm 1/N^{1/2}$, depending on whether the permutation is even or odd. Thus if $PA(1)B(2) \cdot E(N)$ represents a function in which such a permutation has been made, we have as our function

$$\frac{1}{N^{1/2}} \sum \pm PA(1)B(2) \cdots E(N)$$

or, written as a determinant,

$$\frac{1}{N!^{1/2}}\begin{vmatrix} A(1) & A(2)\cdots A(N) \\ B(1) & B(2)\cdots B(N) \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ E(1) & E(2)\cdots E(N) \end{vmatrix}$$

The factor $1/N!^{1/2}$ is inserted in order partly to take care of normalization. If $A, B, \cdots E$ are normalized (as we assume them to be), then if they are also orthogonal, the whole function will be normalized. We do not assume A, B, etc. to be actually orthogonal, but in any case this choice of a factor simplifies the formulas.

We have seen that to each set of one-electron functions $A, B, \cdots E$ corresponds just one antisymmetric function for the whole system. In our perturbation problem, however, we consider a whole group of such antisymmetric functions, and therefore a whole group of sets of one-electron functions. The degeneracy involved arises from two sources: spin degeneracy, and orbital degeneracy. This is a direct consequence of the fact that the quantum numbers of an individual electron are divided into those depending on the orbit, and that depending on the spin, and the fact that the wave function of the electron can be written as a product of a function of the coordinates, and a function of spin.

In the first place, we consider spin degeneracy. Suppose we are given a single set of orbital one-electron functions. Corresponding to this, we have a rather large number of possible arrangements of the spins. For example, if the orbital functions are all different, each spin can be either parallel or antiparallel to the axis, so that if we consider all possibilities there will be 2^N different arrangements, and the same number of unperturbed wave functions. After solving the perturbation problem, these yield a doublet level for one electron ($2^1=2$), a singlet and a triplet for two electrons ($2^2=1+3$), two doublets and a quartet for three electrons ($2^3=2+2+4$), two singlets, three triplets, and a quintet for four electrons ($2^4=1+1+3+3+3+5$), and so on. Or if the orbital functions are not all different, some of these arrangements are not allowed on account of the exclusion principle, each pair of equal functions contributing only one possibility rather than four, so that two equivalent electrons have only a singlet level, two equivalent ones and one other a doublet, two equivalent ones and two others a singlet and triplet, and so on.

Next we consider orbital degeneracy. We must take, not merely one set of one-electron orbital functions, but usually a number of such sets. Each set will have all the possible spin arrangements, so that the number of unperturbed functions which we use can become considerable. We shall find, however, that we can often choose our orbital functions in advance so as to simplify the problem by obtaining groups of terms which do not influence each other. The actual way of choosing the orbital functions is a question about which there might be considerable difference of opinion. In the first place, we could choose functions which are solutions of a central field problem, as is

done in the atomic case, and as Heitler and London[4] have done in discussing molecules. Or second, we could use solutions of the problem of many centers, as Lennard-Jones[5] has done in molecular problems, and as Bloch[6] has done in the problems of metals. In the present paper we shall confine ourselves to the first method, although we do not wish to indicate that the other method is not sometimes valuable. Even if we use only solutions of a central field problem, still it is not obvious which functions we should use. In an atom, it is easy to answer this question: we use functions corresponding to a definite azimuthal quantum number, and a definite component of angular momentum along a fixed direction. The essential reason for doing this is that the total component of angular momentum along a fixed direction is quantized, so that this choice of functions produces a splitting up of the terms into different groups, which do not combine, and which therefore can be treated separately, greatly simplifying the calculation. With diatomic molecules, if the axis is chosen as the axis of figure, we have the same simplifying feature. But with polyatomic molecules, unless they happen to be linear, this is no longer the case. The torques acting on the electrons are such that the component of orbital angular momentum in every direction changes with time, and no longer is quantized. The conventional wave functions, determined by the quantum numbers n, l, m_l, no longer have any particular advantage. We shall as a matter of fact find that in many cases different choices of wave functions will very decidedly simplify the calculation. Examples of this will be pointed out later. The essential idea of using such different wave functions is that in many cases we can choose them so that the lowest state of the molecule can be determined from one set of orbital functions alone, without considering any orbital degeneracy. To do this, however, requires very careful choice of the functions. We shall find in the end that they must be chosen essentially according to the criterion which has been stated by the writer and by Pauling: they must be such as to give as much overlapping as possible with the other electrons to which they are held by valence bonds, and as little as possible with electrons to which they are not held. That is to say, they must be concentrated bond functions. In many cases, too, it is necessary for these lowest states to proceed as Pauling has, using functions in which not merely the component of angular momentum along a fixed axis is not quantized but where even the total angular momentum is not determined. That is, we use functions which are not s, or p, or d electrons, but are mixtures of all these. A criterion like that of Pauling, for getting most concentrated bond functions, would be applied to know which function to use in any particular case. We shall see later by examples just how the functions should be chosen in particular cases.

(3) Matrix Components

Suppose we have two antisymmetric wave functions, one (U) formed from the one-electron wave functions $A \cdots E$, the other (U') from the one-electron

[4] W. Heitler and F. London, Zeits. f. Physik **44,** 455 (1927).
[5] J. E. Lennard-Jones, Trans. Faraday Soc., **25,** 684 (1929).
[6] F. Bloch, Zeits. f. Physik **57,** 545 (1929).

functions $A' \cdots E'$. Suppose also that we have some operator F, whose matrix component we desire between these two functions. Later we may specialize by letting F be the energy, unity, or other quantities. Then by definition, using the formula for antisymmetric wave functions, our matrix component is $\int U^* F U' \, dv = (U/F/U') =$

$$\frac{1}{N!} \int \sum \pm PA^*(1)B^*(2) \cdots E^*(N)F\Big(\sum \pm PA'(1) \cdots E'(N)\Big)dv,$$

where we therefore have a double summation, over permutations in each function. But now on account of the fact that the only operators F which we meet are symmetric in the electrons, we see that each term of the first summation yields the same result, and since there are just $N!$ terms the result can be written as a single sum,

$$\int A^*(1)B^*(2) \cdots E^*(N)F\Big(\sum \pm PA'(1) \cdots E'(N)\Big)dv.$$

Each term of the summation is of the form

$$\int A^*(1)B^*(2) \cdots E^*(N)FA'(1) \cdots E'(N)dv,$$

and such an integral we shall symbolize as

$$(AB \cdots E/F/A' \cdots E').$$

We shall meet such integrals constantly, and shall write our various "exchange integrals" in this form. We can then symbolize our whole matrix component as $\Sigma \pm (AB \cdots E/F/PA' \cdots E')$.

One simplification arises when we introduce the spin part of the wave functions separately, and when F is independent of spin, or of magnetic effects. If then a is the part of the function A depending on coordinates, etc., we have $(AB \cdots E/F/A' \cdots E') = (ab \cdots e/F/a' \cdots e')$ if A and A' have the same spin, and so on down to E and E' having the same spin; but it equals zero otherwise.

In case $AB \cdots E, A' \cdots E'$ are all orthogonal to each other, many simplifications appear, which were met with in the atomic problem, but do not generally appear in the molecular problem. Two forms of operator are of particular interest, those of the form $F = \Sigma_i f_i$, a sum of terms each depending on the coordinates of one electron, and those of the form $G = \Sigma$ (pairs ij) g_{ij}, a sum of terms each depending on the coordinates of a pair of electrons. In this case it is easily shown that the following results hold, where U and U' represent two antisymmetric wave functions:

$$(U/F/U) = \Sigma(a)\ (A/f/A)$$
$$(U/F/U') = (A/f/A'), \text{ if } U' \text{ differs from } U \text{ by just one index, } A \neq A',$$
$$= 0 \text{ otherwise.}$$

Also

$$(U/G/U) = \Sigma \text{ (pairs } AB) \; ((AB/g/AB) - (AB/g/BA))$$

$$(U/G/U') = \Sigma(B \neq A) \; ((AB/g/A'B) - (AB/g/BA')), \text{ if } U' \text{ differs from } U \text{ by one index, } A' \neq A$$

$$= (AB/g/B'A') - (AB/g/\overleftrightarrow{B'A'}), \text{ if } U' \text{ differs from } U \text{ by two indices, } A' \neq A, \; B' \neq B$$

$$= 0 \text{ otherwise.}$$

In these equations,

$$(A/f/B) = \int A(1) f_1 B(1) dv_1$$

$$(AB/g/CD) = \int\int A(1)B(2) g_{12} C(1)D(2) dv_1 dv_2.$$

If in particular F and G do not involve the spins, we have just functions of the coordinates coming into the expressions above: $(A/f/B)$ is zero unless a and b are connected with the same spin, in which case it equals $(a/f/b)$, where a and b are orbital functions, and $(AB/g/CD)$ is zero unless A and C are connected with the same spin, and also B and D, in which case it equals $(ab/g/cd)$. Although in molecular problems we generally have one-electron functions which are not orthogonal to each other, still they do not depart far from orthogonality, and for that reason terms which are entirely absent according to the rules above are likely to be small for molecules. Thus for instance, since energy operators are of the form F and G, the components of energy are small between two functions which differ in respect to more than two electrons.

It is worth while to consider the form which the matrix components of energy will take in actual cases. The energy operator for a molecule with fixed nuclei is

$$H = -\frac{h^2}{8\pi^2 m} \sum_i \nabla_i^2 - \sum_{i\alpha} \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{\alpha\beta} Z_\alpha Z_\beta / r_{\alpha\beta} + \sum_{ij} e^2 / r_{ij}.$$

In this, the summations over i and j are over the electrons, those over α and β are over the nuclei. The Z's represent the nuclear charges, in electronic units, and the r's the distances of separation. We now allow this operator to act on a function $a(1) \cdots e(n)$. In doing this, we note the equations which the functions a, etc., satisfy. These are of the form

$$\frac{+\, h^2}{8\pi^2 m} \nabla^2 a = (V_a - E_a) a$$

where V_a is a potential function for the one electron problem, E_a an energy level. Substituting, we have

$$Ha(1) \cdots e(n) = \Big(-\sum_a (V_a - E_a) - \sum_{i\alpha} Z_\alpha e^2 / r_{i\alpha} + \sum_{\alpha\beta} Z_\alpha Z_\beta / r_{\alpha\beta} + \sum_{ij} e^2 / r_{ij} \Big) a(1) \cdots e(n).$$

All terms but the last are either constants or functions of single electrons, and so form the functions f; the last sum represents a sum over all pairs of electrons, and so is the sum of g's.

When now we multiply this by another wave function, and integrate, we obtain terms of two sorts. First, there are the small terms which result entirely from lack of orthogonality of the functions. Similar terms to these would also be found in the matrix of unity, and in the final calculation most of them will cancel out. For instance, in computing the mean value of a constant term in the energy over any unperturbed function, we must get just this constant itself. Yet this often comes about by having such terms in an energy expression in a numerator of a fraction, and corresponding terms in matrix elements of unity in a denominator, so that finally these terms just balance out. These terms, then, though they must be considered in the actual calculation, are not of particular theoretical interest, and need not be discussed further.

The terms of the second sort are similar to the Coulomb and exchange integrals which Heitler and London found in the problem of the diatomic molecule, or to the similar integrals within the atoms which we meet in complex atomic spectra. Thus for instance if we have the Coulomb integral $(ab \cdots e/H/ab \cdots e)$, the result is essentially similar to a sum of Coulomb interactions between all pairs of electrons in the molecules. With the simple resonance integral, $(ab \cdots e/H/ba \cdots e)$, where the two functions differ just in the interchange of functions a and b, connected with different atoms, the leading terms form just the sort of exchange integral between a and b that Heitler and London would have found if the molecule contained no other electrons. If the two functions differ by a cyclic permutation of three electrons, as $(abc \cdots e/H/cab \cdots e)$, we have an integral which would be zero if the functions were orthogonal, and which will be much smaller than the simple exchange integrals in any case. It is hardly worth while in a general discussion to go more into details about the various integrals. One thing should be noted, however, for the guidance of any one making actual calculations: it is necessary to analyze carefully the exact relations of the functions V_a and the various terms in $1/r$ in the energy. Some of the terms refer to interactions within the various atoms, others to interactions between atoms, and a careful separation of them is essential. It is much safer to formulate the problem in a general way, including all electrons of the problem, as we have sketched here, and then eventually to show that some terms are independent of interatomic distance and lead to atomic energies, than just to start out as if the atoms consisted only of valence electrons surrounding a nucleus of some effective nuclear charge, even though the latter method gives qualitatively the correct interpretation of multiplet levels, valence, and so on.

(4) Solution of the Secular Equation

In the last two sections, we have sketched the method to be used in setting up unperturbed wave functions, and in calculating matrix components of the energy and of unity with respect to them. We are now able to set up

the secular equation for the energy, and the next problem is to try to solve it. The equation is an algebraic one of high order, and without special devices we cannot hope to attack it successfully. In the atomic problem, it was generally possible to find enough special properties of the equation to permit of its complete solution, without any difficulty whatever. In the first place, each unperturbed state was characterized by two quantities, the component of orbital and spin angular momentum along a fixed axis, which we called M_L and M_S respectively, which remained constant when we applied the perturbations. As a result of this, we could divide the states into groups, each with a particular M_L, M_S, and each such group could be treated independently of the others. H had no matrix components from one group to another, so that the secular equation broke up into a product of factors, each connected with one group. This automatic factoring of the equation helped with the solution, but a further principle also was of service. It could be proved by independent methods that all the roots of the partial equation connected with a given M_L, M_S, were also roots of the equations connected with any group with smaller M_L or M_S. Thus we knew some, at least, of the roots of each partial equation, provided we had already solved the equations connected with larger M_L and M_S. As a matter of fact, proceeding in a systematic manner, it was found that in every case discussed, all but one root of each partial equation could be determined in this way. Now when all but one of the roots of an algebraic equation are known, it is very easy to solve for the other one. We can merely use the theorem that the sum of the roots equals the coefficient of the next to the highest power of the unknown, provided the coefficient of the highest power in unity. Thus by subtracting the known sum of all but one root from the known sum of all the roots, we get immediately the desired root. Since our equation is written in the form of a determinant, it can be shown immediately that the desired coefficient, equal to the sum of roots, is simply the sum of all the diagonal elements H_{ii} appearing in the determinant. Thus in the atomic case we were actually able to dispense with the calculation of all elements except these diagonal ones, and we encountered no equations except linear ones, so that all energies were linear functions of the various integrals.

In the molecular problem, the method is not so easy. The orbital angular momentum is no longer quantized, and the only special fact which we have left is that the levels are separated into groups with different values of M_S, resulting in a factoring of the equation into sub-equations, and the occurrence of all the roots of one equation in the next lower equation. The net result of this is that we can break up the terms into groups, each containing all the terms of the same multiplicity. Thus if there is just one term of a given multiplicity, its energy will be given linearly in terms of the various integrals; if there are two the energies will be given as roots of a quadratic, and so on. In other words, for practical purposes we are limited, as far as exact solutions are concerned, to cases where no more than two terms of the same multiplicity occur. For example, suppose our problem is one in which all electrons have different but definite orbital wave functions, and in which the only degeneracy is that of spin. Then two electrons give a singlet and triplet, each

of which we can get explicitly (as Heitler and London did in the case of H_2, an example of this case). Three electrons give a quartet and two doublets, and the quartet comes linearly in terms of the integrals, the two doublets as the two roots of a quadratic. Four electrons give a quintet, which can be obtained, three triplets, which could be found only as the roots of a cubic, and two singlets, the roots of a quadratic. Fortunately the molecular levels of lowest multiplicity are stable, so that with four electrons we can still get the energy of the lowest level explicitly. But with five or six electrons there are five doublets, or five singlets, respectively, and the solution can no longer be found by elementary methods. In diatomic molecules, special properties of symmetry in the nuclei, and other such things can produce a possibility of still further factoring, and can simplify the solution. But in general such methods are not applicable in polyatomic molecules, and we shall therefore not make particular use of them.

Fortunately the cases which we can solve exactly include some important ones, in which we can examine the relative sizes of various terms. When we do this, it appears that certain approximate methods can be legitimately used, when we are interested only in the lowest molecular level. These methods amount to choosing a particular combination of unperturbed functions as the most likely one, by a method suggested by the chemical method of drawing valence bonds, and using as the energy simply the mean value of H averaged over this combined wave function. We shall show that this gives results which are quite satisfactory in the cases where we can check them up, and that it leads in general to physical results concerning energy levels and valence bonds which are of great interest. The special cases will be discussed in the next section, and these general considerations will be described in the concluding section.

(5) Illustrations in Typical Cases

(a) Two atoms, each with one *s* electron

As a first simple illustration, we take the interaction of two atoms each containing a single s electron (H_2, Na_2, NaK, etc.).[7] Let a be the wave function (of coordinates only, not involving spin), of an electron on the first nucleus, b the function of an electron on the second. Since the electrons are s electrons, there is no orbital degeneracy to consider. As a result of spin degeneracy, there are four unperturbed functions: In this table, + means that the component of the electron's spin along an arbitrary axis is $+\frac{1}{2}h/2\pi$, and − means that it is $-\frac{1}{2}h/2\pi$. A total spin of 1 means really $1h/2\pi$. Now a triplet has

	Spin of a	Spin of b	Total spin
I	+	+	1
II	+	−	0
III	−	+	0
IV	−	−	−1

[7] This problem has been discussed in detail by N. Rosen, Phys. Rev. **38,** 255 (1931).

three degenerate levels, of total spin 1, 0, −1, and a singlet has one level, of spin 0. Hence we have a triplet and a singlet. Further, if we work out matrix components of energy and unity, we find that there are no components between states of different spin, so that I, IV stand all by themselves, and II and III are grouped together. Now we can work out our matrix components according to the rules of section 3. We have

$$H_{\mathrm{I,I}} = (ab/H/ab) - (ab/H/ba)$$
$$d_{\mathrm{I,I}} = (ab/1/ab) - (ab/1/ba) = 1 - (ab/1/ba),$$

if a and b are normalized. Thus we have as one factor of the secular equation merely

$$((ab/H/ab) - (ab/H/ba)) - W(1 - (ab/1/ba)) = 0,$$

or

$$W = \frac{(ab/H/ab) - (ab/H/ba)}{1 - (ab/1/ba)}.$$

This is evidently the energy of the triplet. Next we compute the other components:

$$H_{\mathrm{II,II}} = (ab/H/ab) = H_{\mathrm{III,III}}$$
$$H_{\mathrm{II,III}} = H_{\mathrm{III,II}} = -(ab/H/ba)$$
$$d_{\mathrm{II,II}} = d_{\mathrm{III,III}} = 1$$
$$d_{\mathrm{II,III}} = d_{\mathrm{III,II}} = -(ab/1/ba).$$

Then we have the following secular equation between states II and III:

$$\begin{vmatrix} (ab/H/ab) - W & -(ab/H/ba) + (ab/1/ba)W \\ -(ab/H/ba) + (ab/1/ba)W & (ab/H/ab) - W \end{vmatrix} = 0,$$

or $((ab/H/ab) - W)^2 - (-(ab/H/ba) + (ab/1/ba)W)^2 = 0$. This equation can be factored at once into

$$((ab/H/ab) - (ab/H/ba) - (1 - (ab/1/ba))W) \times$$
$$((ab/H/ab) + (ab/H/ba) - (1 + (ab/1/ba))W) = 0.$$

Setting the first factor equal to zero, we obtain just the triplet solution already found. In fact, if we did not know how to factor or otherwise solve our quadratic, we could have divided it through by this linear factor, and the resulting linear equation would have given us the singlet directly. This gives as the singlet energy

$$W = \frac{(ab/H/ab) + (ab/H/ba)}{1 + (ab/1/ba)}.$$

When we examine the meaning of the integrals, we see that $(ab/H/ab)$ is Heitler and London's H_1, $(ab/H/ba)$ is their H_2, and $(ab/1/ba)$ is their S^2. Thus these results agree exactly with the ones which they derive.

It is worth while to solve also for the coefficients determining the correct linear combinations of wave functions. We find of course that I and IV give directly two of the three components of the triplet. Substituting the energy values into the equations for II and III, we find that except for a normalizing factor, the third function connected with the triplet is II+III, and the singlet function is II−III. It is to be noted that this result seems at first sight strange, when compared with the well-known fact that the triplet functions are antisymmetric in the coordinates of the two electrons, while the singlet functions are symmetric. We might at first sight expect the signs to be reversed. But if we actually put in the functions of coordinates and of spin, we find that the singlet function II−III is really symmetric in the coordinates, antisymmetric in spin, so that it is all right.

(b) Three electrons, with only spin degeneracy

The preceding case was really the general one of two electrons, with orbital wave functions a and b, with only spin degeneracy. Next we consider the case of three such electrons, with functions a, b, and c. We expect a quartet and two doublets. There are eight unperturbed functions. State I and

	Spin of a	Spin of b	Spin of c	Total spin
I	+	+	+	3/2
II	+	+	−	1/2
III	+	−	+	1/2
IV	−	+	+	1/2
V	−	−	+	−1/2
VI	−	+	−	−1/2
VII	+	−	−	−1/2
VIII	−	−	−	−3/2

VIII by themselves give two of the four states of the quartet. II, III, IV give a cubic, one of whose roots gives another state of the quartet, and the other two roots give the two doublets. Similarly V, VI, VII yield the fourth state of the quartet, and the other two states of the doublets. We have then

$$H_{I,I} = (abc/H/abc) - (abc/H/bac) - (abc/H/acb) - (abc/H/cba) + (abc/H/bca) + (abc/H/cab)$$

$$d_{I,I} = 1 - (abc/1/bac) - (abc/1/acb) - (abc/1/cba) + (abc/1/bca) + (abc/1/cab).$$

The energy of the quartet is then

$$W = \frac{(abc/H/abc)-(abc/H/bac)-(abc/H/acb)-(abc/H/cba)+(abc/H/bca)+(abc/H/cab)}{1-(abc/1/bac)-(abc/1/acb)-(abc/1/cba)+(abc/1/bca)+(abc/1/cab)}$$

It is worth noting that if the functions a, b, c are nearly orthogonal, the last two terms of numerator and denominator will be small compared with the others, since they correspond to interchange of three electrons. Thus to an

approximation we may write the formula without these terms. Of if we wish an even rougher approximation, we may leave out the terms in the denominator altogether, as we could if the functions were really orthogonal, obtaining a formula for the quartet

$$W = (abc/H/abc) - (abc/H/bac) - (abc/H/acb) - (abc/H/cba),$$

or the first term, minus the terms obtained by making each possible interchange of two electrons.

To investigate the doublet terms, we must consider the secular equation between II, III, and IV. We have

$$\begin{aligned}
H_{\mathrm{II,II}} &= (abc/H/abc) - (abc/H/bac)\\
H_{\mathrm{III,III}} &= (abc/H/abc) - (abc/H/cba)\\
H_{\mathrm{IV,IV}} &= (abc/H/abc) - (abc/H/acb)\\
H_{\mathrm{II,III}} &= (abc/H/cab) - (abc/H/acb)\\
H_{\mathrm{III,IV}} &= (abc/H/cab) - (abc/H/bac)\\
H_{\mathrm{II,IV}} &= (abc/H/cab) - (abc/H/cba).
\end{aligned}$$

The matrices of unity are just the same, with 1 substituted for H. In the last formula, we have used the fact that $(abc/H/bca) = (abc/H/cab)$. This follows from the following two steps: $(abc/H/bca) = (cab/H/abc)$, since from definition we can make any permutation of the first set of indices, if only we make an identical permutation of the second set at the same time; and $(cab/H/abc) = (abc/H/cab)$, since the matrices are Hermitian and real.

Instead of trying to solve the cubic equation between II, III, and IV, we shall adopt a method which we shall find useful in many cases. We introduce four linear combinations of the three functions, which we shall call A, B, C, and D, by the equations

$$\begin{aligned}
A &= 1/2^{1/2}(\mathrm{II} - \mathrm{III})\\
B &= 1/2^{1/2}(\mathrm{III} - \mathrm{IV})\\
C &= 1/2^{1/2}(\mathrm{IV} - \mathrm{II})\\
D &= \tfrac{1}{2}(\mathrm{II} + \mathrm{III} + \mathrm{IV}).
\end{aligned}$$

These four functions cannot of course be linearly independent; as a matter of fact, as one immediately sees, $A+B+C=0$. Thus one can use three independent ones, as A, B, and D, for setting up a new secular equation. When we compute the matrices of H and of unity with respect to these functions, we discover immediately that all matrices between D and any one of the other three functions are zero. That means that our secular equation is already factored: one energy level is that obtained directly from D, or $H_{D,D}/d_{D,D}$, and the other two are roots of a quadratic obtained, say, from the functions A and B. Now the first energy value proves to be just the energy of the quartet, so that we see that D is the wave function of the quartet. The wave functions for the doublets are then two orthogonal linear combinations of A and B

(or A and B and C, which comes to the same thing). To set up the secular equation between A and B, we make use of one fact: since $A+B+C=0$, we have at once

$$H_{AA} + H_{AB} + H_{AC} = 0$$
$$H_{AB} + H_{BB} + H_{BC} = 0$$
$$H_{AC} + H_{BC} + H_{CC} = 0.$$

Eliminating from these equations, we have $H_{AB}=\frac{1}{2}(H_{CC}-H_{AA}-H_{BB})$. That is, we can write our nondiagonal elements of energy in terms of the diagonal elements. The same result holds for the matrix of unity. Now substituting in the secular equation, and using the abbreviations

$$H_{AA} = P,\ H_{BB} = Q,\ H_{CC} = R,\ d_{AA} = p,\ d_{BB} = q,\ d_{CC} = r,$$

we easily find that the solutions of the quadratic are

$$W = \frac{P(p-q-r)+Q(-p+q-r)+R(-p-q+r)}{p^2+q^2+r^2-2pq-2qr-2pr}$$
$$\pm \frac{2(P^2qr+Q^2pr+R^2pq+PQr(r-p-q)+QRp(p-q-r)+PRq(q-p-r))^{1/2}}{p^2+q^2+r^2-2pq-2qr-2pr}.$$

This equation takes an interesting form in the case where we can neglect the lack of orthogonality of the functions II, III, IV. For then we have $p=q=r=1$, and the limiting form is

$$W = \frac{P+Q+R}{3} \pm \frac{2}{3}(P^2+Q^2+R^2-PQ-QR-PR)^{1/2}$$
$$= \frac{P+Q+R}{3} \pm \frac{2}{3}(\tfrac{1}{2}((P-Q)^2+(Q-R)^2+(R-P)^2))^{1/2}.$$

It is easily found that the diagonal elements of the matrix of H, required in these formulas, are

$$H_{AA} = P = (abc/H/abc) + (abc/H/acb) - \tfrac{1}{2}((abc/H/bac) + (abc/H/cba)) - (abc/H/cab)$$
$$H_{BB} = Q = (abc/H/abc) + (abc/H/bac) - \tfrac{1}{2}((abc/H/acb) + (abc/H/cba)) - (abc/H/cab)$$
$$H_{CC} = R = (abc/H/abc) + (abc/H/cba) - \tfrac{1}{2}((abc/H/acb) + (abc/H/bac)) - (abc/H/cab).$$

The formulas for p, q, r, are the same with unity in place of H. In the limiting case where $p=q=r=1$, we can then use $P-Q=3/2((abc/H/acb)-(abc/H/bac))$, etc., obtaining[8]

[8] F. London, Zeits. F. Electrochem. **35**, 552 (1929); Sommerfeld Festschrift, Hirzel, p. 104.

$$W = (abc/H/abc) - (abc/H/cab) \pm \{\tfrac{1}{2}(((abc/H/acb) - (abc/H/bac))^2 + ((abc/H/bac) - (abc/H/cba))^2 + ((abc/H/cba) - (abc/H/acb))^2)\}^{1/2}.$$

The method we have used deserves a certain amount of comment for its physical interest. The function A is essentially II–III. Now if the electron a were removed to a large distance from b and c, so that we had large interaction just between b and c, we should have the case of a diatomic molecule, and from the preceding section we see that this function would give just the singlet state of that molecule, the one givng strongest molecular binding. Thus A corresponds essentially to a valence bond between electrons b and c. Similarly B corresponds to a bond between a and b, and C to a bond between a and c. The real situation appears as a combination of these, taking some of the character of each. Generally one of the three bonds will appear much stronger than the others, and then the real wave function is much nearer the function A, B, or C, as the case may be, as we can find by actually working out the transformation coefficients.[9] The energy in such a case takes on a particularly simple form. We can get at this in either of two ways. First, we can expand the quadratic, regarding certain interaction integrals as being large, others small. For example, if the electron a were removed to a large distance, the integral $(abc/H/acb)$ would still be large, for it is essentially an exchange integral between b and c, but the integrals $(abc/H/bac)$ and $(abc/H/cba)$ would be small. Expanding the quadratic, taking for simplicity the case $p=q=r=1$, we have

$$W = (abc/H/abc) - (abc/H/cab) \pm \{(abc/H/acb) - \tfrac{1}{2}((abc/H/bac) + (abc/H/cba))\}$$

The diatomic molecule bc by itself would have the energy $(abc/H/abc) \pm (abc/H/acb)$, where the a in the integrals plays a purely formal role. Thus we see that the addition of the electron a has two results: first, the small term $(abc/H/cab)$, coming from cyclic permutation of electrons, is introduced. This is unimportant. But second, the exchange integral $(abc/H/acb)$ between the electrons b and c is diminished by half the integrals $(abc/H/bac)$ and $(abc/H/cba)$ between a and b and c respectively. For example, if we take the negative sign, the interaction integral between b and c would normally give an attraction between these atoms. Then the interaction between a and the other atoms will be one of repulsion, but this repulsion will be only half as great as if b and c were not bound into a molecule. Physically, then, if a univalent atom approaches a diatomic molecule formed of two univalent atoms, the single atom will repel the molecule. On the other hand, if the atom approaches too closely, the approximation no longer holds, and it may even become bound to one of the atoms of the molecule, liberating the remaining atom of the molecule in the process, and resulting in a chemical reaction. The necessary energy which the molecule must have to rise over the hill of potential to the valley corresponding to the other form of molecule is the heat of activation, as has been shown by Eyring and Polanyi.[10]

[9] Compare W. Heitler, Phys. Rev. **38**, 243 (1931).

[10] Eyring and Polanyi, Zeits. physik. Chem. **B12**, 279 (1931).

The second way in which we may get at the approximate energy, when the wave function is very nearly one corresponding to a pure valence bond is to notice that the functions A, B, C correspond exactly to these bonds, and that by first order perturbation theory the diagonal energy values of these states give the best approximations to the energy. Thus for the bond between atoms a and b, we have the state A, and we see that the diagonal energy $H_{AA}=P$ is exactly the same that we found by expanding the quadratic. More accurately, we should take the energy to be $H_{AA}/d_{AA}=P/p$. By taking advantage of this fact, we can avoid the necessity of expanding in quadratics entirely in many cases, although of course not in finding activation energies, for in that problem we must be able to pass continuously from one limiting case to another. For discussing a single molecule, however, the linear formula is in general sufficient, as we shall see as we progress. And we may well state in words the characteristic of the wave function and energy level which we have to express this case. The wave function is made up of the two unperturbed functions for which the electrons to be bound have opposite spins, the two functions being added with opposite signs. And the energy is the sum of the Coulomb interaction $(abc/H/abc)$, the exchange term $(abc/H/acb)$ between the electrons being bound, diminished by half the exchange term between the remaining electron and the two bound in the molecule, and further corrected by the cyclic term. As we progress, we shall find this general situation characteristic of valence binding.

(c) Four electrons, with only spin degeneracy

The case of four electrons, with functions a, b, c, d is similar in most respects to that of three. There are one quintet level, three triplets, and two singlets, so that we cannot get the triplets in explicit form without solving a cubic. Since the levels in which we are most interested are the singlets, we limit ourselves to solving for them. There are sixteen unperturbed functions, of which we list those having positive or zero total spin. The function I is

	Spin of a	Spin of b	Spin of c	Spin of d	Total spin
I	+	+	+	+	2
II	+	+	+	−	1
III	+	+	−	+	1
IV	+	−	+	+	1
V	−	+	+	+	1
VI	+	+	−	−	0
VII	+	−	+	−	0
VIII	+	−	−	+	0
IX	−	+	+	−	0
X	−	+	−	+	0
XI	−	−	+	+	0

a quintet function. II, III, IV, and V give a biquadratic equation, of which one root is the quintet energy, the others the three triplet energies. Finally VI–XI lead to a secular equation of the sixth degree, having as roots the roots of the biquadratic, and also the two singlet energy levels. If we now

evaluate the fourth power and sixth power equations, as polynomials in W, we must find that the sixth power one is divisible by the fourth power one, leading to a quadratic equation. We can greatly simplify the calculation, however, if we introduce at the outset seven linear combinations of the functions VI . . . XI. These combinations may be denoted as follows:

$$A: \tfrac{1}{2}(\text{VI} - \text{VIII} - \text{IX} + \text{XI})$$
$$B: \tfrac{1}{2}(\text{VIII} - \text{VII} - \text{X} + \text{IX})$$
$$C: \tfrac{1}{2}(\text{VII} - \text{VI} - \text{XI} + \text{X})$$
$$D: 1/2^{1/2}(\text{VII} - \text{X})$$
$$E: 1/2^{1/2}(\text{VIII} - \text{IX})$$
$$F: 1/2^{1/2}(\text{VI} - \text{XI})$$
$$G: 1/6^{1/2}(\text{VI} + \text{VII} + \text{VIII} + \text{IX} + \text{X} + \text{XI})$$

As with three electrons, the functions A, B, C are not independent, but instead $A+B+C=0$. When now we compute the matrix components of H and of unity with respect to the functions $A \cdots G$, using for this purpose the components between the functions VI $\cdots$ XI, we find that the functions fall into three groups: A, B and C, D, E, and F, and G, such that the matrix components between the groups are exactly zero. In this way we have an automatic factoring of the secular equation into a quadratic, a cubic, and a linear equation. Simple discussion shows that two combinations of A, B, and C correspond to the singlets, D, E, and F to the triplets, and G to the quintet level. To solve for the singlets, then, we need only use the quadratic secular equation between states A and B.

Since $A+B+C=0$, we have just the same situation that we did in the case of three electrons. All the calculation goes through as before, and we need not even rewrite the solutions of the quadratic equation. The only difference is in the values of the diagonal energies, H_{AA}, H_{BB}, H_{CC}, or P, Q, and R. These are

$$\begin{aligned}
P = {} & (abcd/H/abcd) + (abcd/H/cbad) + (abcd/H/adcb) \\
& - \tfrac{1}{2}((abcd/H/bacd) + (abcd/H/dbca) + (abcd/H/acbd) + (abcd/H/abdc)) \\
& - \tfrac{1}{2}((abcd/H/cabd) + (abcd/H/bdca) + (abcd/H/dbac) + (abcd/H/acdb) \\
& + (abcd/H/bcad) + (abcd/H/dacb) + (abcd/H/cbda) + (abcd/H/adbc)) \\
& + ((abcd/H/badc) + (abcd/H/cdab) + (abcd/H/dcba)) \\
& + ((abcd/H/bcda) + (abcd/H/dabc)) \\
& - \tfrac{1}{2}((abcd/H/bdac) + (abcd/H/cdba) + (abcd/H/cadb) + (abcd/H/dcab)) \\
Q = {} & (abcd/H/abcd) + (abcd/H/bacd) + (abcd/H/abdc) \\
& - \tfrac{1}{2}((abcd/H/cbad) + (abcd/H/dbca) + (abcd/H/acbd) + (abcd/H/adcb)) \\
& - \tfrac{1}{2}((abcd/H/cabd) + (abcd/H/bdca) + (abcd/H/dbac) + (abcd/H/acdb) \\
& + (abcd/H/bcad) + (abcd/H/dacb) + (abcd/H/cbda) + (abcd/H/adbc))
\end{aligned}$$

$$+ ((abcd/H/badc) + (abcd/H/cdab) + (abcd/H/dcba))$$
$$+ ((abcd/H/cdba) + (abcd/H/dcab))$$
$$- \tfrac{1}{2}((abcd/H/bcda) + (abcd/H/bdac) + (abcd/H/cadb) + (abcd/H/dabc))$$

$$R = (abcd/H/abcd) + (abcd/H/dbca) + (abcd/H/acbd)$$
$$- \tfrac{1}{2}((abcd/H/cbad) + (abcd/H/adcb) + (abcd/H/bacd) + (abcd/H/abdc))$$
$$- \tfrac{1}{2}((abcd/H/cabd) + (abcd/H/bdca) + (abcd/H/dbac) + (abcd/H/acdb)$$
$$+ (abcd/H/bcad) + (abcd/H/dacb) + (abcd/H/cbda) + (abcd/H/adbc))$$
$$+ ((abcd/H/badc) + (abcd/H/cdab) + (abcd/H/dcba))$$
$$+ ((abcd/H/bdac) + (abcd/H/cadb))$$
$$- \tfrac{1}{2}((abcd/H/bcda) + (abcd/H/dabc) + (abcd/H/cdba) + (abcd/H/dcab)).$$

The values of p, q, and r are just the same, with unity in place of H.

On account of the rather formidable nature of these formulas, it is worth while describing the physical nature of the terms. First in each case comes the Coulomb interaction $(abcd/H/abcd)$. Next come six terms connected with the six possible resonance interchanges of pairs of electrons. These six terms alone are large and important. Two of them in each case have positive coefficients, and hence produce binding, since the integrals themselves are generally negative. They correspond to valence bonds between two pairs of electrons: the pairs ac and bd in state A, ab and cd in B, ad and bc in C. Thus as with the three electron case we may say that each of our three states corresponds to one of the three possible ways of drawing the valence bonds, and the leading terms in the energies P, Q, R give just the sum of the binding energies for the two bonds, in each case. The remaining four resonance terms are for the other four possible bonds, and they come with coefficients $-1/2$, showing that the other pairs repel, but only half as strongly as if they were by themselves. The next group of eight terms come from cyclic permutations of three electrons, and the last nine come from permutations in which all four electrons change. Thus these last terms are all small, and we need not consider them in detail. As far as the broad outlines are concerned, we see that the diagonal energies follow the same principles as with three electrons. The solutions as well follow the same general lines. The real wave functions are combinations of A, B, and C, so that they do not correspond exactly to any one way of drawing the valence bonds. Nevertheless, in many cases one way will be much nearer the truth than any other, and in such cases one of these three functions will be a good approximation, and we may use the corresponding diagonal energy, as for example P/p, as a good approximation to the truth. It is worth while noticing how the wave function corresponding to a given way of drawing the valence bonds is constructed. Let us take, for instance, the function B, where the bonds are between a and b, and between c and d. Then in the first place the function is made up of the separate functions VII, VIII, IX, and X, in each of which a and b have spins opposite to each other, and similarly c and d have spins opposite to each other. Then these four functions are

combined with such coefficients ± 1 that whenever we go from one function to another by interchanging the spins of a and b, or of c and d, we go to a function of opposite sign. This description proves to be a general one for the correct function to use in a case where there are definite valence bonds drawn in a certain way.

(d) More than four electrons, with only spin degeneracy

With more than four electrons, we cannot solve the problem of spin degeneracy, even to the extent of obtaining the levels of lowest multiplicity. For example, with five electrons, there are five doublet levels, and with six electrons there are five singlets. The energies would then be roots of an equation of the fifth degree, and it is useless even to set it up. On the other hand, we have noted in the case of four electrons that there can be cases (very important ones in actual practice), where the energy of the lowest state can be found as the mean energy of a wave function connected with one definite way of drawing valence bonds. And this can be done in general: whenever one method of drawing the bonds is very much more likely than any other, we can use this method for writing the energy in terms of the exchange integrals, to a good approximation. To set up the wave function, we proceed as follows: First, we draw the valence bonds, between definite pairs of electrons. All electrons are understood to be paired off, if the molecule has an even number of electrons, and all but one if it has an odd number. Then we take all the 2^N wave functions (if N is the number of complete pairs) for which the two electrons of any pair have opposite spins. We combine these functions with coefficients ± 1, such that when we pass from one function to another by interchanging the spins of a pair of electrons, we go to a function of opposite sign. This sum, divided by the square root of the number of terms for convenience in normalization, is the required function expressing the valence binding. The energy connected with the state is the ratio of the mean value of H over the state to the mean value of unity. Each of these quantities involves integrals connected with all sorts of permutations of the electrons. But if we confine ourselves to the most important terms, namely those in which no electrons change, or in which only a pair of electrons is interchanged, then the mean values are easily described. First there is the Coulomb term in the energy, or the term 1 in the matrix of unity. Then there are the interchange terms, with coefficients $+1$, between all the various pairs (N such terms) of electrons bound together. As far as these terms go, then, it is just as if all thepairs were independent of each other, and as if the energy required to dissociate the whole molecule were the sum of the energies required to dissociate its various bonds if they were by themselves. But the other possible interchange terms, between all other pairs of electrons, come in with coefficients $-1/2$, so that we interpret it as saying that all other pairs which are not definitely bound by valence forces repel each other, but by only half the amount they would exert if they were by themselves in the repulsive configuration. The further terms, in cyclic and other interchanges, come in with smaller coefficients, in different ways depending on the number of electrons.

In the general case, we can go even further than setting up these linear expressions for energy. We can work out a case where the valence bonds are not definite, but where they are intermediate between two of the definite cases we have considered. For them the correct wave function is a combination of two of these approximate functions, and we have only a quadratic equation for the energy. The simplest case is that where four electrons, a, b, c, d, are bound in some way intermediate between our three possible cases $ab\ cd$, $ac\ bd$, $ad\ bc$, but in which there are also many other electrons, which however are bound to each other in perfectly definite ways. This is the problem which we should meet in a rather general case of a chemical reaction, where two molecules approach, each one breaks into two halves by the parting of a single valence bond, and the parts recombine in either of the two possible ways. Here, just as with the four electron problem, we can set up three functions A, B, and C, corresponding to these three ways of drawing the bonds. These functions are set up, and their energies computed, according to the rules we have just described. But now, just as with four electrons, we find that these functions are not independent, but rather that $A+B+C=0$. Thus all the calculation of the preceding sections can be applied to this case, we obtain the energy as the root of the same quadratic, and the only difference is in the value of the diagonal energy values P, Q, and R. When we substitute in the correct values, we find that only those terms involving interchanges between the four electrons a, b, c, d remain inside the radical, so that this looks just as in the four electron problem. Outside the square root sign come the interchange integrals between other pairs of electrons, just as if we were using a linear solution rather than a quadratic one.

(e) Two electrons, one *s* and one *p*

The problem of two atoms, one containing an s and one a p electron, involves orbital as well as spin degeneracy. There are three possible p wave functions, and we must consider how this affects the energy levels. Further, we have a choice as to what three functions to take. For on account of the degeneracy, we may take any three linear combinations of the functions with which we start. First, however, we shall choose the conventional p functions. These may be denoted as p_+, p_0, p_-, having respectively the components 1, 0, 1 − of angular momentum along the fixed axis. We naturally choose this axis as the line on which the nuclei are placed. Then we have twelve unperturbed functions: for p_+s we have four on account of spin degeneracy, for p_0s four, and for p_-s four more. But now there is a fortunate fact: just as with atoms, the component of orbital angular momentum about the axis of figure is a constant of the motion, and the matrix components of energy, and of unity, between two states with different values of this quantity, are zero. In other words, the matrix components vanish between states in different groups of four, and the secular equation automatically factors into three factors, each involving four states. Each of these yields a problem exactly like that without orbital degeneracy which we have considered before, and therefore results in a singlet and a triplet, the formulas being as before. As a matter of fact, how-

ever, we shall not have three singlets and three triplets, but only two of each, for the states p_+s and p_-s will yield the same energies, although different wave functions. Thus these will result in an orbital degeneracy which persists, at least until further perturbations are taken into account, and the states are II states. The final conclusion, then, is that we will have from p_+s and p_-s $a^1\Pi$ and $a^3\Pi$, and from p_0s $a^1\Sigma$ and $a^3\Sigma$. To tell which of these is the lowest state, we must consider the magnitudes of the exchange integrals, for the energies of the singlet states are essentially given by these exchange integrals, and the one which has the largest negative value will correspond to the most stable level. But now these exchange integrals are such things as $\int a(1)b(2)\cdot H b(1)a(2)d\tau$. That is, they involve in their integrands the quantities $a(1)b(1)$ and $a(2)b(2)$, as if they were charge densities. Now if the functions a and b do not overlap at all—that is, if there is no region of space where they are simultaneously of considerable size—the integrand will be everywhere small, and the integral will be small. In general, the more they overlap, other things being equal, the larger will they be. But now the functions p_0 and s will overlap far more than p_+ and s, or $p-$ and s. The reason is found in the spatial arrangement of the functions, as has been described in an earlier paper. p_0 is concentrated along the axis joining the p and the s electron, so that it has its maximum intensity in just the place where it can overlap the s. On the other hand, p_+ and p_- have their concentration along the plane normal to the axis, and they are zero right on the axis. Thus we see that the $^1\Sigma$ state will be the most tightly bound, and will be the normal state. And in the course of our discussion, we have seen that the p electron will tend to take up that particular degenerate state which points out along the direction toward the other electron with which it is in valence binding. To get the actual energy, we have the formula, from our discussion of the two electron problem.

(f) Two atoms, each with a p electron

Here we have more degeneracy than before. Both electrons can be in p_+, or both in p_-. These will yield $^1\Delta$ and $^3\Delta$, with very weak binding. Then either one can be in p_+ and the other p_0, or either one in p_- and the other in p_0. This degeneracy would result in two $^1\Pi$, and two $^3\Pi$, and we should have to solve quadratics to determine the energy, were it not for the symmetry of the problem, by which we can actually separate into functions symmetric and antisymmetric in the nuclei. Finally we have the problem of no component of orbital angular momentum, with three possible orbital arrangements: p_+p_-, p_0p_0, or p_-p_+. As a result of this we should have three $^1\Sigma$ and three $^3\Sigma$. We should have to solve a cubic to get either of these, except that symmetry in the nuclei permits factoring into a linear and quadratic term. But the states p_+ and p_- have very little overlapping, while p_0 and p_0 overlap a great deal. Thus the latter state corresponds to a much lower energy, and we may anticipate that one of the wave functions, the one connected with the lowest energy, will correspond very closely to this particular orbital arrangement. We should be able therefore to obtain a fairly good approximation by taking just the singlet and triplet coming from p_0p_0 alone, getting strong binding

for the singlet. Here again, then, we can say that for the valence bond the correct p electrons are those which point in the direction of the other electron.

Bartlett[11] has computed the integrals in this case of two p electrons, and in general finds verification of the statements of the preceding paragraph. In one respect his results are in extraordinary disagreement with what we should expect: he finds the exchange integral between the two p_0 states in the two atoms to be positive rather than negative, so that he finds the triplet, rather than the singlet, state to lie lower. This is so entirely in disagreement with expectation that we must question the result, and we cannot regard this question as being closed until further calculation is made. As a possible source of explanation of this discrepancy, however, we may note that Bartlett's calculation is for hydrogen, with nuclear charge 1, whereas in ordinary molecules the effective nuclear charge would be decidedly greater than 1. It seems altogether possible that the integral could depend enough on nuclear charge to change sign, and be negative with these larger charges.

(g) Two atoms, one with two equivalent p electrons, the other with an s electron

The atom with two equivalent p electrons furnishes an atomic problem, and we consider it first, assuming the atom with the s electron to be removed to infinity. This procedure is not necessary, but it is useful in that it suggests an improved method of dealing with the degeneracy of the p electrons, in this sort of problem. First we tabulate the various exchange integrals which we shall need. Being an atomic problem, we can go much further toward calculating them than we can without great difficulty in the molecular case. They can all be obtained from the tables in the paper on complex spectra, where they are given as combinations of certain integrals F^0 and F^2, integrals over the radial part of the wave functions of the electrons. The three degenerate functions in which we are interested may be symbolized in the interest of brevity by $+, 0, -$. Then from the paper mentioned we derive the values

$$(+\,+/H/+\,+) = F^0 + 1/25F^2, \text{ which we may symbolize } (1,\ 1/25)$$
$$(+\,0/H/+\,0) = (1,\ -2/25);\quad (+\,0/H/0\,+) = (0,\ 3/25)$$
$$(+\,-/H/+\,-) = (1,1/25);\quad (+\,-/H/-\,+) = (0,\ 6/25)$$
$$(00/H/00) = (1,\ 4/25).$$

Now we may tabulate all the possible states we can set up, considering only the orbital degeneracy. These states may be tabulated as follows:

I	+	+
II	+	0
III	+	−
IV	0	0
V	−	0
VI	−	−

[11] J. H. Bartlett, Phys. Rev. **37**, 507 (1931).

The state I is connected with $M_L=2$, II has it equal to 1, III and IV each have 0, V has -1, VI has -2. Hence all states may be considered separately, and have no matrix components of energy between them, except III and IV, which must be grouped together. When now we consider the spin degeneracy, I and VI will lead only to singlet levels, on account of the exclusion principle. The energy will be $(++/II/++)=(--/II/--)=(1,\ 1/25)$. The levels are two of the five sub-levels of ^1D, and this then is the energy of that state. II and V, being nondegenerate problems with nonequivalent electrons, will each give a singlet and a triplet, the singlet having energy$(+0/II/+0)$ $+(+0/II/0+)=(1,\ 1/25)$, and accounting for two more of the sublevels of ^1D, and the triplets having energy $(+0/II/+0)-(+0/II/0+)=(1,\ -5/25)$, accounting for two sublevels of the ^3P. Finally III will lead to a singlet and a triplet, and IV to a singlet only, on account of the exclusion principle. But we cannot get these energies without solving a cubic between the states. One singlet is of course the remaining level of ^1D, the triplet is the remaining level of ^3P, and the other singlet is ^1S, so that as a matter of fact we can easily find the energy: we know the sum of roots, and also all the roots but one, so that we can subtract. Thus, considering only states of $M_S=0$, we have three states, of diagonal energies $(+-/II/+-)$, $(+-/II/+-)$, $(00/II/00)$. Adding, and subtracting the energies of ^1D and ^3P, we at once have for ^1S the energy $(1,\ 10/25)$. But this procedure, while feasible with the atomic problem, will not work with the molecular one. For there we cannot assume that the energy values will be repeated in problems with different values of M_L, and the device of subtraction is no longer open to us to any such extent as with atoms. Further, these very levels with $M_L=0$ are the ones that lead to stable molecular binding, and for that reason they are the most important ones for the molecular case. Thus if we retain the $+$, 0, $-$ p functions, we will meet real difficulty when we try to solve the molecular problem. Fortunately it is possible, however, to introduce other p functions which overcome this trouble, and which prove in general to be much more suited to calculation in molecular problems.

To set up these new functions, we start with the expression of p_+, p_0, p_- in rectangular coordinates. If the axis is chosen as the z axis, then these functions are

$$p_0 = zf(r)$$

$$p_+ = \frac{x+iy}{2^{1/2}} f(r)$$

$$p_- = \frac{x-iy}{2^{1/2}} f(r).$$

But now we can immediately introduce three linear combinations of these,

$$p_x = xf(r)$$

$$p_y = yf(r)$$

$$p_z = zf(r),$$

which prove to be the desired functions. We can obtain the exchange integrals with respect to them immediately, using their expression as combinations of the previous functions, and we find

$$(xx/H/xx) = (yy/H/yy) = (zz/H/zz) = (1, 4/25)$$
$$(xy/H/xy) = (yz/H/yz) = (zx/H/zx) = (1, -2/25)$$
$$(xy/H/yx) = (yz/H/zy) = (zx/H/xz) = (xx/H/yy) = (yy/H/zz)$$
$$= (zz/H/xx) = (0, 3/25).$$

All other coefficients are zero, such as $(xx/H/xy)$, or $(xy/H/xz)$. Using these functions, we have the following states, considering only orbital degeneracy:

I	x	x
II	y	y
III	z	z
IV	x	y
V	y	z
VI	z	x.

When we investigate the matrix of the energy, we see that I, II, III must all be considered together as a group, since the matrix components between them do not vanish. On the other hand, each of the states IV, V, and VI forms a separate group by itself, without components to any other states. On account of the exclusion principle, I, II, III will between them yield three singlets, and examination shows that these are the ^1S, and two sublevels of ^1D. IV, V, and VI give each a singlet and a triplet, each leading to one of the levels of ^1D and one of ^3P. Thus we have for ^1D the energy $(xy/H/xy)+(xy/H/yx) = (1, 1/25)$, and for ^3P $(xy/H/xy)-(xy/H/yx) = (1, -5/25)$. Finally by subtraction we find $^1S:{}^1S+2{}^1D = 3(1, 4/25)$, $^1S = (1, 10/25)$. Since we must use subtraction here as before, it would seem at first sight as if we should be no better off then we were before. But this is not true, for it appears that the states xy, yz, zx are the ones concerned in the lowest states of the molecule, and the orbital degeneracy is entirely removed from these states.

We may now pass to the molecular problem, using the $x\ y\ z$ functions. We assume the other atom to be located along the x axis, and denote its wave function by X. Again considering only orbital degeneracy at first, we have the following table of functions:

I	x	x	X
II	y	y	X
III	z	z	X
IV	x	y	X
V	y	z	X
VI	z	x	X

Now when we investigate the matrix of the energy, we still find, as we did before, that IV, V, and VI may be considered by themselves, although I, II, and III must be grouped together. The reason is a very general one of symmetry. Let us for instance take the substates of IV and V for which all spins are parallel, so that we need not consider them. Then

$$H_{\mathrm{IV,V}} = (xyX/H/yzX) - (xyX/H/zyX) - (xyX/H/Xzy) - (xyX/H/yXz) + (xyX/H/Xyz).$$

The terms most likely to give something different from zero will be those in $1/r_{ij}$ in H. Take these for example in the first integral. This is $\int x(1)y(1)y(2)z(2)X(3)X(3)(1/r_{12}+1r_{23}+1/r_{31})dv_1dv_2dv_3$. But now the first integral is zero, because interchanging the z coordinates of both electrons 1 and 2 changes the sign of the function $z(2)$, leaving everything else unchanged, so that each contribution to the integral is balanced by an equal and opposite one. The second term is zero for the same reason, and the third on account of the possibility of interchanging the y coordinates. We note that this argument is dependent on having the function X symmetrical with respect both to y and z, so that this electron must be on the x axis.

As with the atom, then, we have three states, IV, V, and VI, without orbital degeneracy, and three others, I, II, and III, which must be considered together. These last three give rise to three doublet levels, which prove to be $a^2\Sigma$, and the two sublevels of $a^2\Delta$. On account of the fact that two roots coincide, we can solve the cubic equation, and it proves to be the case that these levels are high up, as we would expect from the fact that they come from the higher atomic levels. Thus if we are interested only in the lower molecular levels, we may confine ourselves to the states IV, V, VI. Each of these is a problem of three electrons with spin degeneracy, but without orbital degeneracy. The solution, then, can be carried out as in section (b), and we obtain in each case a quartet and two doublets, the latter as the two roots of a quadratic. The problems IV and VI lead evidently to the same energy levels, and examination shows them to be Π levels, while V yields Σ levels. A simple discussion shows that the Π levels will be lower than the Σ ones, the lower $^2\Pi$ being the lowest level of all. For illustration, let us take assumed values for the exchange integrals, and actually work out the energies.

As an example, we choose OH, for which some of the quantities are approximately known. The O atom, of course, has four p electrons rather than two, but the energy formulas for the case where two are lacking from the closed shell should be the same as when only two are present. It is known that the heat of dissociation of OH into O and H is of the neighborhood of 5.4 volts.[12] Further, the energy difference between the ^3P and ^1D of the O atom is about 2 volts.[13] Let us now make most crude assumptions, merely to get orders of magnitude. We shall suppose that we can neglect all lack of orthogonality, that the energy comes entirely from resonance terms, so that we can

[12] R. S. Mulliken, Phys. Rev. **33,** 739 (1929).
[13] R. Frerichs, Phys. Rev. **36,** 398 (1930).

neglect Coulomb interactions, and that we can neglect exchange terms from cyclic permutations of electrons. We shall need, then, values for a number of exchange integrals. First, we can derive the value of $(xyX/H/yxX) = (yzX/H/zyX) = (zxX/H/xzX)$ from the 2 volt separation between the terms of the atom. For this separation should be twice the integral, which is therefore about 1 volt. Next, we note that the other exchange integrals fall into two classes: $(xyX/H/Xyx)$ and $(xzX/H/Xzx)$, in which X and x electrons are in resonance, and $(xzX/H/xXy)$, $(xzX/H/xzX)$, $(yzX/H/yXz)$, etc., in which an X and either a y or z electron are in resonance. Now the X and x electrons overlap greatly, while the X and y or z overlap much less. Thus the integrals of the first group are large numerically, those of the second group small. Both are negative, presumably. In the absence of calculation, we make the rough approximation that the second is 1/5 of the first. Then to get the correct heat of dissociation we may take the integrals of the first sort to be about -5 volts, and those of the second sort -1 volt, for the value of distance of separation which gives the minimum of energy. Having values for our integrals, we may now use our solutions of the three electron problem to find the approximate energies, for the assumed distance of separation. From states IV or VI, we have a $^4\Pi$ and two $^2\Pi$'s. The energy of the first should be $-(xyX/H/yxX) - (xyX/H/Xyx) - (xyX/H/xXy) = -(1) - (-5) - (-1) = 5$ volts, corresponding to large repulsion. For the doublet states, we must solve a quadratic: the energies are

$$\pm \{\tfrac{1}{2}(((xyX/H/yxX) - (xyX/H/Xyx))^2 + ((xyX/H/Xyx) - (xyX/H/xXy))^2 + ((xyX/H/xXy) - (xyX/H/yxX))^2)\}^{1/2}$$

$$= \pm \{\tfrac{1}{2}[(1+5)^2 + (-5+1)^2 + (-1-1)^2]\}^{1/2} = \pm 28^{1/2} = \pm 5.3 \text{ volts.}$$

Thus the one doublet lies as high as the quartet, but the other one corresponds to attraction, of about the right amount, and represents the normal state. In the same sort of way, the energy of the $^4\Sigma$ is $-1+1+1=1$ volt, and of the two $^2\Sigma$'s $\pm\{\tfrac{1}{2}[(1+1)^2+(-1+1)^2+(-1-1)^2]\}^{1/2} = \pm 2$ volts. One doublet is attractive, but not nearly as much so as the $^2\Pi$ state, so that it would correspond to an excited level.

The lowest state, then, comes from the problem in which we have a resonance interaction between the X electron of the one atom, and the x electron of the other, which can overlap with it a great deal. No such overlapping is possible in the other cases, and there is not nearly as tight binding. In this lowest state, the binding between X and x is so strong that we can speak of a definite valence bond between them, and it is interesting to see if the approximate formula for energy based on the assumption of a definite bond is applicable. This gave for the energy the interaction integral concerned in the bond, decreased by half the sum of all other interaction integrals. Thus in this case it would be $-5-\tfrac{1}{2}(1-1) = -5$ volts, which is a fairly good approximation to the root of the quadratic, -5.3 volts. Thus in this case we should be justified, if we were not looking for very accurate values, in using

this approximation, and saying that the valence bond was definitely between the electrons which have large overlapping, the X and x electrons.

It is interesting to consider what our Π levels do in the case of large internuclear separation. There the leading term in the energy is the atomic integral $(xyX/H/yxX)$, which is independent of distance. Noticing how this enters the expressions for energy, we see that the $^4\Pi$, and the lower $^2\Pi$, go to the lower, ^3P state of the atom, while the other $^2\Pi$ goes into the ^1D of the atom. At large distances, the energy is given to a next approximation by using our linear functions. Thus the energy of the lowest state is given by $-(xyX/H/yxX)$ $+\frac{1}{2}((xyX/H/Xyx)+(xyX/H/xXy))$. The binding energy, $(xyX/H/Xyx)$, comes in only with a factor $\frac{1}{2}$. But more significant than this is the fact that the interaction energies between X and x and y both come in with the same sign, so that they both contribute to the binding. In the other limiting case, on the other hand, when the binding between X and x is the large term, these two interactions come in with opposite sign, so that while X is bound to x, it is in repulsive interaction with y. It is easy to see, therefore, that the qualitative nature of interactions can change depending on whether molecular interaction is large or small compared with atomic energy differences. The whole theory of directional valence, as developed by the present writer and by Pauling, is a phenomenon connected with strong valence binding. In that case, definite interaction energies come in with positive sign, and contribute to binding. Our object is then to adjust the orbital wave functions, by making concentrated bond functions, so as to make these interaction integrals as big as possible. On the other hand, all other interactions come in as repulsions, so that it is necessary to make them as small as possible. By applying these principles, we are led to the idea of sharply concentrated wave functions for valence binding, sticking out in definite directions in space. If the valence binding were weak compared with atomic energies, on the other hand, there would not be this necessity, for there are no definitely defined bonds which give attraction with others leading to repulsion. Thus in these cases we should not be led to concentrated wave functions, and to directional effects. Now it is very significant that Heitler in his discussion has always limited himself to consideration of a single atomic energy level. That means essentially that he assumes the atomic interactions to be so large that he need consider only the lowest state, as if the other atomic states lay much further up. In this case we would expect no such directional effects as with strong valence bonds, and it is interesting to note that Heitler has not inferred the existence of such effects from his calculations.

(h) Three atoms, one with two equivalent p electrons, the others with an s electron each

This problem could serve as a simplified model of the H_2O molecule, just as the preceding one resembled the OH. In general, we shall find the problem too difficult to get accurate solutions. There is a special case, however, in which we can carry through the calculations, and we assume that special case to start with. Fortunately it is not far from the truth. This is the case in

which the lines joining the monovalent atoms to the divalent one make an angle of 90° with each other. Assuming this case, we let one s electron be along the x axis, the other along y, and we denote their functions by X and Y. We use the x, y, z p functions, as before. Then considering orbital degeneracy alone, we have just the same six functions as in the previous case. Moreover, the addition of the extra atom, so long as it is just on the y axis, does not interfere with the vanishing of matrix components between the groups of states IV, V, and VI. As before, then, I, II, and III lead to a group of high levels, which we must consider together. The problem is no longer linear, and we cannot use the notations Σ, Π, Δ, etc., but can denote states only by their multiplicities. We can thus only say that from these states we have three singlets and three triplets, and we can be quite sure that they will be high, repulsive levels. Next we consider the states IV, V, VI. The lowest level will come from state IV, with x and y, p electrons, for then we have the possibility of two strong bonds. The states V and VI allow only one strong bond each, and so must be much less strongly attractive levels, and we may neglect them. Now the problem of x, y, X, Y electrons is a four electron problem with only spin degeneracy, and therefore leads to two singlet states, three triplets, and a quintet, of which one singlet will be the lowest. The energy of this singlet comes as the solution of a quadratic, as we have already found, but just as with the preceding case, we can often use the linear approximation to the quadratic. To investigate this, we may put in rough approximate values for the integrals in H_2O, as we did for OH.

Neglecting the same terms that we did for OH, we need a number of exchange integrals to determine our energies. We will assume the same values of the integrals which have already occurred in OH, as follows:

$$(xyXY/H/yxXY) = 1$$
$$(xyXY/H/XyxY) = (xyXY/H/xYXy) = -5$$
$$(xyXY/H/YyXx) = (xyXY/H/xXyY) = -1.$$

The only other integral which we need is $(xyXY/H/xyYX)$, the exchange integral between the two hydrogen atoms. This we can get approximately from the band spectrum of hydrogen, for its energy is given directly in terms of this integral. To get the distance between the two hydrogens, we note that the OH distance in H_2O, according to all calculations, is about 1A, so that the distance between the hydrogens, assuming the right angled model, is 1.41A. This is about twice the distance of equilibrium for two hydrogens interacting with each other, and the exchange energy at this distance is about -0.8 volts.

We now have for our energy the value $-\{\frac{1}{2}((-5-5+1+1)^2+(-1-1-1+0.8)^2+(1-0.8+5+5)^2)\}^{1/2}=-9.3$ volts. This is not far from the energy indicated for dissociation of H_2O into H, H, and O. Thermochemical data would lead to a value of about 10 volts. Thus we see that our general calculation is fairly good, in spite of its many crude features. It is now interesting to note that here again the valence bonds are strong enough so that we can use our linear approximation. This would give for the energy $-5-5$

$-\frac{1}{2}(-1-1+1-0.8) = -9.1$ volts, quite a good approximation to the quadratic. This should be a fairly representative case for the magnitudes in actual compounds, so that it seems as if we were justified in using this approximation in general.

For angles other than 90° between the bonds, we can no longer get such a valid solution. For then our nondiagonal terms between states IV, V, and VI no longer vanish on account of symmetry, and we cannot consider the states as leading to independent problems. There is one other case which we can solve properly, however: that where the angle is 180°, the linear molecule. In that case we still can separate our problem, and states IV or VI lead to identical energy levels, and give the lowest state. Suppose our two s electrons are on the x axis, and denote them by X, $-X$. Then we have

$$(xyX - X/H/yxX - X) = 1$$

$$(xyX - X/H/Xyx - X) = (xyX - X/H/- XyXx) = -5$$

$$(xyX - X/H/xXy - X) = (xyX - X/H/x - XyX) = -1$$

$$(xyX - X/H/xy - XX) = 0 \text{ practically,}$$

the last because the H atoms are so far apart. Then the energy of the lowest singlet is $-\{\frac{1}{2}((-5-1+5+1)^2+(-5-1-1-0)^2+(1+0+5+1)^2)\}^{1/2} = -7$ volts. In other words, the right angled arrangement is decidedly more stable than the linear one. For this linear model, we cannot use our approximate method, for no one way of drawing the valence bonds is preferred over any other: we cannot say whether the X or the $-X$ hydrogen is bound to the x p function of the oxygen.

For angles near 90° we can have resort to an approximate method to indicate the general form of the curve of energy against angle. Even if the nondiagonal terms between our state IV and other states are no longer zero, they will still be small, for small deviations of the angle. Thus we may still use a first order calculation, taking the unperturbed wave function as formed in IV, and averaging the correct energy over it. To be more precise, we assume the functions X and Y to be located, not just on the x and y axes, but on axes in the same plane, but inclined by an angle ϕ to these axes, so that they make an angle of $90°+2\phi$ with each other. We still have the same six states, considering orbital degeneracy, and the lowest state will come from IV, but now with some contributions from the other state. We neglect these contributions, however, solving merely the problem of state IV by itself. The only difference from our previous calculation comes then in the values of the exchange integrals. If previously the integral $(xyXY/H/XyxY)$ was -5 volts, and $(xyXY/H/xXyY)$ was -1 volts, then we can easily show that in the present case, with the new definition of X, we have $(xyXY/H/XyxY) = -5\cos^2\phi - 1\sin^2\phi$, and $(xyXY/H/xXyY) = -1\cos^2\phi - 5\sin^2\phi$. We do this by noting, for example, that the function x can be written as a linear combination of two functions, one pointing along the direction at the angle ϕ, the other along the direction at right angles to it. Each of these functions is just like an

ordinary p function, and has interaction integrals with the s electrons just as if the latter were along the x axis. When we put in these expansions, we at once get the expressions mentioned. Now we are ready to substitute in the energy formula. For convenience, we use only the linear formula, which we have already shown to be sufficient. We know all terms except the exchange integral between X and Y, which will depend on ϕ because that affects the distance between hydrogen atoms. We now have for our energy

$$2(-5\cos^2\phi - 1\sin^2\phi) - \tfrac{1}{2}(2(-1\cos^2\phi - 5\sin^2\phi) + 1 + (xyXY/II/xyYX)).$$

This can be put in the form $-9.5+12\sin^2\phi-\frac{1}{2}(xyXY/II/xyYX)$. Of course, it reduces properly for $\phi=0$. On the other hand, it is not correct for the linear model, which we get by putting $\phi=45°$; in this case it reduces to -3.5, rather than the correct value -7. Thus we see that it will give in general too high energy values, as of course we can see from general principles, for the mean value of the energy over an incorrect wave function always will give too high energy. Nevertheless, the general form of the variation with angle is certainly a suggestion of the correct law: surely the energy increases as the angle deviates from a right angle, and presumably the correct law could at least be well approximated by a $\sin^2$ law. We can then say at least qualitatively what to expect. If the hydrogen exchange integral $(xyXY/II/xyYX)$ could be neglected, the stable position of the molecule would be with the right angle form. But actually this integral decreases numerically as the hydrogens move farther apart, or as the angle increases. Since it appears in the form of a repulsion between the hydrogen atoms, we shall find equilibrium at an angle slightly larger than a right angle. The p valences by themselves have a definitely directional effect, but this is superposed on an ordinary repulsion of the atoms which are not bound by valence forces.

(i) Four atoms, one with three equivalent p electrons, the others with an s electron each.

Here we have a model of the NH_3 molecule, for example. We shall not discuss it in as great detail as we have used in the preceding cases, for the principles are similar. Again the only cases which we can treat correctly are those in which the three monovalent atoms make angles of 90° with each other. But as before this is the stable position if we can neglect the repulsion of these atoms for each other, and if we consider the repulsions the angles are slightly increased. Taking account of orbital degeneracy, and taking the s atoms to have wave functions X, Y, and Z, we have the following states:

I $xxyXYZ$

II $xyyXYZ$

III $yyzXYZ$

IV $yzzXYZ$

V $zxxXYZ$

VI $zzxXYZ$

VII $xyzXYZ$

The states like $xxxXYZ$ are forbidden by the exclusion principle. Now as before, when the states XYZ are really along the axes, the state VII has vanishing matrix components to all other states. It is from this last state that we expect to get the lowest level of the molecule. It is the only one which allows strong bonds between X and x, between Y and y, and between Z and z. In this connection, we can use a principle which we did not mention with the other cases, but which was equally applicable there. In such a state as $xxyXYZ$, the two electrons x form essentially a closed subshell, and cannot take part in valence binding. Only the single electron y is free to form a bond, and naturally in these functions there can be no great binding energy, and they will lead to high and probably repulsive levels of the molecule. Thus we are led to the problem $xyzXYZ$, a six electron problem without orbital degeneracy. We cannot get its exact solution, but we can use our approximate method valid in cases of strong binding, and that should be satisfactory here. According to this, the energy is the sum of the exchange integrals between X and x, between Y and y, and between Z and z ,which are all large and negative, and diminished by half the sum of all other exchange integrals. Those between X and y and z and the other similar ones, will reduce the energy, as in the preceding problem. Those between X and Y, and the other similar ones, will represent the repulsion between the hydrogen atoms. There are, then, no essential differences between this problem and those we have already discussed.

(j) Five atoms, one with four s and p electrons, the others with an s electron each

This problem could represent the methane molecule, CH_4. A new situation enters here, in that we may not confine ourselves to p electrons only. For then we should have to have for the atom a combination, say, like $xxyz$, necessarily having two electrons in a closed group, and leaving only two free for forming bonds. We must then consider the possibility that some of the electrons in the large atom are in s orbits. Since two s electrons would again form a closed group, defeating our purpose, we have but one possibility, namely that there be one s electron and three p's. Then by analogy with our previous case we expect the lowest state to come from the configuration in which the four electrons in the large atom were all in different states, as $s\ x\ y\ z$, so that all could take part in binding. With our four other atoms, we then have an eight electron problem, in which we hope to be able to neglect orbital degeneracy. We cannot do this in general, however, any more than we could with the other problems except in special cases, for particular positions of the other atoms. For we have nondiagonal terms of the energy, between our function and others in which two s or p electrons are in the same wave function. Our object, then, is so to move around our other atoms, and also to make such linear combinations of the functions s, x, y, z, that these nondiagonal terms

will become as small as possible, and the solutions of our problem without orbital degeneracy will approach as closely as possible to the real solution of the problem. Now we may regard this in either of two ways. First, if we can really make the nondiagonal terms zero by such manipulation, then when we have done it we shall be justified in neglecting orbital degeneracy, and the solution we get will be correct. But second, if we leave out of account these nondiagonal terms from the beginning, we can always solve for the lowest level coming from our one set of orbital functions. This energy level will vary as we manipulate the positions and orbital wave functions of the electrons, and by the general variation principle we know that the lowest possible energy which it can get will be the correct energy value. Thus we simply manipulate the orbital functions to make the energy a minimum, and use this minimum property as a criterion for the correctness of the functions. This process, to take care of spin degeneracy by exact or approximate solution of the perturbation problem, but to treat orbital degeneracy by a variation method, may be considered to be the real essence of the scheme suggested by the present writer and by Pauling for the treatment of molecular problems.

When now we try to make the energy of our lowest state a minimum, we have very definite information to assist us. First, the energy will surely be lower if we can form definite strong valence bonds than otherwise. If we can, then we know that the lowest state of the problem of spin degeneracy can be approximately set up, and that the energy will be a sum of the exchange integrals connected with the bonds, diminished by half the sum of all other exchange integrals. All these exchange integrals connected with molecular interactions are presumably negative. Then we have a perfectly definite way to make our energy low: We must manipulate the functions in such a way as to make the exchange integrals connected with our definite bonds as big numerically as possible, and to make all others as small as possible. But this is just what is accomplished by making the orbital functions as concentrated in space as possible, and by making the two functions involved in a bond overlap as much as possible. By this maximum overlapping and concentration, the desired integrals will be made large on account of their large integrand, and those which we wish to be small will do so, since the very concentrated orbital functions will keep out of the way of other functions, overlapping them very little, and not contributing greatly to other exchange integrals. Thus the requirement of concentrated bond functions, each strong in a restricted region but keeping out of the way of others, which has been emphasized by the writer and by Pauling, is just the requirement necessary to make our energy a minimum, and hence to result in an approximation near the true solution.

In particular, for four combinations of s and p functions, those which most nearly possess the desired property are the tetrahedral ones, described in the previous paper. Let us then introduce these functions, in place of $sxyz$. We must still move around the four univalent atoms, if we want to make the energy a minimum. They must be so placed that one overlaps each of the four tetrahedral functions. This definitely fixes them in a tetrahedral arrangement.

When we have done this, the energy will be made up of the attractive terms binding each hydrogen to its corresponding electron in the carbon; the repulsive term between each hydrogen and all the other carbon electrons; and the repulsions of the hydrogens for each other. Of course, we will also be interested in finding the energy of the molecule when the hydrogen atoms do not have just these positions, in order to investigate vibrational frequencies. Then we must simply move the hydrogens, and compute the energy by the same formulas for the different orbital functions. It is entirely likely, however, that if the hydrogens are slightly displaced, it would prove that a slight compensating displacement of the oxygen functions would reduce the energy. We can imagine that four functions could be set up, not pointing just to the corners of a regular tetrahedron, but in slightly different directions, which would be more advantageous in this case. In a detailed theory this possibility would have to be investigated, and in any case those orbital functions used which gave the lowest energy.

It is quite worth while considering what our lowest energy level will do as the hydrogen atoms are removed from the carbon. At first we should say that it would go into the ^5S level of the atom, the lowest level of the configuration $sxyz$. But this presumably will not be the case, for we have the possibility of a state of the same nature going into the ^3P level of the configuration s^2xy, a lower level, and we know that levels of the same character do not cross. Thus our lowest level will gradually change its properties, as the distance of separation is increased, until finally it will have the correct properties for this ^3P atomic state. Our method will not give a correct description of this whole process. Still, on account of the term in the Coulomb interaction energy which gives essentially the interaction within the atom, our solution will show the level built up as we have done it going to a high energy at large separation, and we should find that by changing the orbital functions by going to the s^2p^2 configuration we could reduce the energy. It is thus in the spirit of the variation method that at each distance of separation we should seek the compromise between these which gives the lowest energy, and treat that as giving the correct description of the state. It is worth while noting that this sort of situation is very common: very often the electronic configuration present in molecular binding at small distances of separation is not that characteristic of the atomic level into which the molecule would disintegrate adiabatically. Lack of knowledge of this fact has been the cause of much misunderstanding.

(6) General Methods for Valence Bonds

In the course of the illustrations in the last section, we have been developing several general principles for use in discussing molecular binding which are worth describing separately. By use of these methods, it is believed that approximate solutions for the lowest states of most molecules may be obtained, accurate enough for rough discussion of chemical problems and of band spectra. In the first place, we make in this method a characteristic

difference in treatment between orbital and spin degeneracy. The treatment of spin degeneracy is based on an approximate solution of the perturbation problem in which we have spin degeneracy without orbital degeneracy. This solution is valid in cases where there are strong and unambiguous valence bonds; that is, where the electrons can be all divided into pairs, such that the exchange integral between the two electrons of a pair is large, but those between electrons not forming a pair are small. It states approximately that the energy is a sum first, of the Coulomb energy; then of the sum of the exchange integrals over all pairs forming bonds; finally of the sum, with coefficient $-\frac{1}{2}$, of all other exchange integrals. That is, the electrons very definitely form bonds from pairs of electrons, rather than just having bonds in an indefinite way between atoms, as Heitler has assumed. And the two electrons in a pair result in attraction, but each electron is in repulsive interaction with every other electron except the one with which it is paired, although these repulsions are diminished to half the value they would have had if the electron were not bound in a shared electron pair. It is worth while noting that, for use in problems of chemical reaction, we have a somewhat more general solution than this, in which we can follow through in detail the process of breaking apart of a single bond in each of two molecules, and of joining together the remaining parts in either of the two possible ways to form other molecules.

We have found it most practicable to treat orbital degeneracy, not by the perturbation method at all, but by the variation method. This rests essentially on the hypothesis that it is possible to find a set of orbital functions, one for each electron, such that the lowest energy level of the problem of spin degeneracy connected with these orbital functions is a good approximation to the lowest state of the problem. We have seen cases where we could find such functions, others where we could do it approximately, though perhaps not exactly. No doubt as more cases are examined in detail, many will be found where the hypothesis is justified, but also very probably some will be found where it is not, and where our method is not applicable. It seems likely that all simple problems of molecules with only single bonds will fall into this scheme, but probably at least some cases of double and triple bonds, as for example the rather anomalous case of the lowest state of O_2, will require special treatment. Other cases which we surely could not treat by the general method would be those like C_6H_6, the benzene ring, where an ambiguity between two ways of drawing the valence bonds seems to be an essential feature of the structure. But if our hypothesis is justified, then we may proceed by varying the orbital functions to try to find the lowest energy level. On account of the expression for energy in terms of exchange integrals mentioned above, the way to do this is very definitely to set up concentrated bond orbital functions, in order to make the desired exchange integrals large, and all others small. This in turn leads to functions very definitely localized in space, with definite directional properties. When we have found such functions, by the methods suggested by Pauling, or by straightforward variation of the energy,

we may then use the formulas developed in the present paper to find the actual energy of the molecule, deriving the necessary exchange integrals either from calculation based on atomic models, or partly on experimental material from band spectra of simpler molecules. This method, which suggests a definite and quite feasible procedure for dealing with a great variety of molecules, should surely be applied to many cases, and should result in chemical and physical information of considerable value.

ALLOWED LEVELS FOR EQUIVALENT (*s, p, d, f*) ELECTRONS WITH (*j j*) COUPLING

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Abstract

The allowed levels for equivalent (*s, p, d, f*) electrons with (*jj*) coupling are given in Tables I, II, III, IV, respectively.

THE allowed levels for equivalent (*s, p, d, f*) electrons with (*jj*) coupling are given in Tables I, II, III, IV, respectively. The levels for (*s, p, d*) electrons are taken from Table I, page 258, "The Structure of Line Spectra"

Table I. *Equivalent (s) Electrons.*

No. of Equiv. (*s*) Electrons	j_i 1/2	j_k	J
s^1	1		1/2
s^2	2		0

Table II. *Equivalent (p) Electrons.*

No. of Equiv. (*p*) Electrons	j_i 1/2	j_k 3/2	J
p^1	1	0	1/2
	0	1	3/2
p^2	2	0	0
	1	1	1 2
	0	2	0 2
p^3	2	1	3/2
	1	2	1/2 3/2 5/2
	0	3	3/2
p^4	2	2	0 2
	1	3	1 2
	0	4	0
p^5	2	3	3/2
	1	4	1/2
p^6	2	4	0

by Pauling and Goudsmit, McGraw-Hill 1930. On the same page is outlined the method of computation.

The coupling scheme for so-called "(*jj*) coupling" is

$$\{(l_1s_1)(l_2s_2)\cdots(l_is_i)\} = \{j_1j_2\cdots j_i\} = J$$

where the interaction between the l, s vectors of an electron is large compared to the interaction of that electron with its neighbors. This interaction energy for a given electron is proportional to the cosine of the included angle between l and s. It is a minimum when the cosine is minus one and l antiparallel

TABLE III. *Equivalent (d) Electrons.*

No. of Equiv. (d) Electrons	j_i 3/2	j_k 5/2	J
d^1	1	0	3/2
	0	1	5/2
d^2	2	0	0 2
	1	1	1 2 3 4
	0	2	0 2 4
d^3	3	0	3/2
	2	1	1/2 3/2 $(5/2)^2$ 7/2 9/2
	1	2	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ 9/2 11/2
	0	3	3/2 5/2 9/2
d^4	4	0	0
	3	1	1 2 3 4
	2	2	$(0)^2$ 1 $(2)^4$ $(3)^2$ $(4)^3$ 5 6
	1	3	0 $(1)^2$ $(2)^2$ $(3)^3$ $(4)^2$ 5 6
	0	4	0 2 4
d^5	4	1	5/2
	3	2	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ 9/2 11/2
	2	3	$(1/2)^2$ $(3/2)^3$ $(5/2)^4$ $(7/2)^3$ $(9/2)^3$ 11/2 13/2
	1	4	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ 9/2 11/2
	0	5	5/2
d^6	4	2	0 2 4
	3	3	0 $(1)^2$ $(2)^2$ $(3)^3$ $(4)^2$ 5 6
	2	4	$(0)^2$ 1 $(2)^4$ $(3)^2$ $(4)^3$ 5 6
	1	5	1 2 3 4
	0	6	0
d^7	4	3	3/2 5/2 9/2
	3	4	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ 9/2 11/2
	2	5	1/2 3/2 $(5/2)^2$ 7/2 9/2
	1	6	3/2
d^8	4	4	0 2 4
	3	5	1 2 3 4
	2	6	0 2
d^9	4	5	5/2
	3	6	3/2
d^{10}	4	6	0

to s, a maximum when l and s are parallel. The energy of an atom composed of such (jj) electrons is, to a first approximation, equal to the sum of the energies of the electrons individually. Therefore it is to be expected, for a given number of electrons, that the lowest J-group will occur when all the electrons have their minimum allowed energy. That is, when there are a maximum number of $j_i = j$ min. Similarly, the highest J-group will occur when there is a maximum number of $j_i = j$ max. The lowest J-group in the first half of a subgroup will be the highest in the last half; the highest J-group in the first half, lowest in the second half.[1] The order of the J's within a group is

[1] In comparing the J's from (jj) coupling with those from (ls) coupling on page 156 of Pauling and Goudsmit "The Structure of Line Spectra" McGraw-Hill, 1930, it was noted that (1) d^5 $^4(SDFGI)$ should be $^2(SDFGI)$, (2) f^6 $^3(PDF\text{——})$ should be $^3(PDF\text{——})$. These values in
6 9 6 5 9
the original table of Gibbs, Wilber, and White, Phys. Rev. **29,** 790 (1927) are correct.

TABLE IV. *Equivalent (f) electrons.*

No. of Equiv. (f) electrons	j_k 5/2	j_k 7/2	J
f^1	1	0	5/2
	0	1	7/2
f^2	2	0	0 2 4
	1	1	1 2 3 4 5 6
	0	2	0 2 4 6
f^3	3	0	3/2 5/2 9/2
	2	1	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ 13/2 15/2
	1	2	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ 15/2 17/2
	0	3	3/2 5/2 7/2 9/2 11/2 15/2
f^4	4	0	0 2 4
	3	1	$(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ 7 8
	2	2	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	1	3	0 $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	0	4	0 $(2)^2$ $(4)^2$ 5 6 8
f^5	5	0	5/2
	4	1	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ 13/2 15/2
	3	2	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ 19/2 21/2
	2	3	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ $(19/2)^2$ 21/2 23/2
	1	4	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ 19/2 21/2
	0	5	3/2 5/2 7/2 9/2 11/2 15/2
f^6	6	0	0
	5	1	1 2 3 4 5 6
	4	2	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	3	3	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ $(9)^2$ $(10)^2$ 11 12
	2	4	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ $(9)^2$ $(10)^2$ 11 12
	1	5	0 $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	0	6	0 2 4 6
f^7	6	1	7/2
	5	2	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ 15/2 17/2
	4	3	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ $(19/2)^2$ 21/2 23/2
	3	4	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ $(19/2)^2$ $(21/2)^2$ 23/2 25/2
	2	5	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ $(19/2)^2$ 21/2 23/2
	1	6	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ 15/2 17/2
	0	7	7/2
f^8	6	2	0 2 4 6
	5	3	0 $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	4	4	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ $(9)^2$ $(10)^2$ 11 12
	3	5	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ $(9)^2$ $(10)^2$ 11 12
	2	6	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	1	7	1 2 3 4 5 6
	0	8	0
f^9	6	3	3/2 5/2 7/2 9/2 11/2 15/2
	5	4	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ 19/2 21/2
	4	5	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ $(19/2)^2$ 21/2 23/2
	3	6	$(1/2)^2$ $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ $(15/2)^2$ $(17/2)^2$ 19/2 21/2
	2	7	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ 13/2 15/2
	1	8	5/2
f^{10}	6	4	0 $(2)^2$ $(4)^2$ 5 6 8
	5	5	0 $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	4	6	$(0)^2$ $(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ $(7)^2$ $(8)^2$ 9 10
	3	7	$(1)^2$ $(2)^2$ $(3)^2$ $(4)^2$ $(5)^2$ $(6)^2$ 7 8
	2	8	0 2 4
f^{11}	6	5	3/2 5/2 7/2 9/2 11/2 15/2
	5	6	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ $(13/2)^2$ 15/2 17/2
	4	7	1/2 $(3/2)^2$ $(5/2)^2$ $(7/2)^2$ $(9/2)^2$ $(11/2)^2$ 13/2 15/2
	3	8	3/2 5/2 9/2
f^{12}	6	6	0 2 4 6
	5	7	1 2 3 4 5 6
	4	8	0 2 4
f^{13}	6	7	7/2
	5	8	5/2
f^{14}	6	8	0

uncertain. In the tables, the lowest groups are listed first, and the J's within the group according to magnitude. Exponents indicate more than one J of the same magnitude.

It is suggested that (jj) coupling may be of use, not only in atomic spectra, but in the structure of the nucleus.

THE ZEEMAN EFFECT IN THE ORTHO-HELIUM BAND SPECTRUM

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Abstract

Resolved and partially resolved Zeeman patterns have been obtained at high dispersion for ortho-helium bands of the types $nd\delta,{}^3\Delta \rightarrow 2p\pi,{}^3\Pi$; $nd\pi,{}^3\Pi \rightarrow 2p\pi,{}^3\Pi$; and $nd\sigma,{}^3\Sigma \rightarrow 2p\pi,{}^3\Pi$. For small values of rotational energy, these patterns agree with the theoretical predictions for a case b' molecule. Departure from these predictions, which increases with n, K, and $l-\lambda$, is noted in all of the above bands. Patterns of some levels of large rotational energy approximate the predctions for a case d' molecule. This departure is in agreement with predictions and observations of the energy changes incident to the uncoupling of the orbital angular momentum of the excited electron from the molecular axis. Thus, the Zeeman effect affords a method of tracing the progress of this uncoupling phenomenon. Evidence is given that the line $Q(9)$ of the band $4p\pi,{}^3\Pi^{(0)} \rightarrow 2s\sigma,{}^3\Sigma^{(0)}$ has a triplet structure without field.

Introduction

Theoretical Expectations

A NUMBER of authors[1] have discussed the energy changes occurring in a molecule when the coupling of the electronic orbital angular momentum to the electric axis is varied. They have pointed out that marked energy changes should occur in light molecules when this coupling is changed from the condition of rigid coupling to that of partial or total uncoupling. It has been further pointed out that such uncoupling of the angular momentum should be most pronounced for large values of the total quantum number, n, of the excited electron, for large values of the rotational quantum number, K, and should become more obvious with increasing difference between the orbitual angular momentum quantum number, l, of the excited electron, and its projection on the electric axis, λ. Several investigators[2] have reported evidence of uncoupling phenomena in accordance with these predictions in the ortho-helium band spectrum, which is theoretically a triplet spectrum ($S=1$), and also in the parhelium spectrum ($S=0$).

If the coupling in the helium molecule is rigid, the orbital angular momentum of the excited electron is so coupled to the electric axis that its projection thereon, λ, is a true quantum number.[3] Mulliken and Monk[4] have shown that the triplet structure in the ortho-helium bands is detectable only

[1] Cf. W. E. Curtis, Trans. Faraday Soc. **25**, 694 (1929), for full references.

[2] W. Weizel, Zeits. f. Physik **52**, 175 (1928), and G. H. Dieke, Zeits. f. Physik **57**, 71 (1929).

[3] Cf. R. S. Mulliken, Reviews of Modern Physics **2**, 97 et seq., Jan., 1930 and **2**, 506, Sept., 1930 for a complete discussion.

[4] R. S. Mulliken and G. S. Monk, Phys. Rev. **34**, 1530 (1929).

in the $2p\pi$, $^3\Pi$ state and that even this structure disappears in a weak magnetic field (i.e., the Paschen-Back effect becomes total at a low value of the magnetic field). Hence the bands in a strong magnetic field may be treated as if they were singlet bands. This case of triplet bands which behave like singlet bands has been classified under case b'.[3] The energy of a case b' singlet state in a magnetic field of strength H is well known to be [5,6]

$$\Delta E_{\text{mag}} = \frac{\mu_1 H M \Lambda^2}{K(K+1)} \tag{1}$$

where M is the magnetic quantum number, K the rotational quantum number, $\Lambda = \lambda$ for the present case, and $\mu_1 = eh/4\pi mc$. Curtis and Jevons[7] and Mulliken and Monk[4] have reported observations upon the Zeeman effect in some $s\sigma$, $^3\Sigma \rightarrow 2p\pi$, $^3\Pi$ ortho-helium bands. The resolved patterns are in agreement with the case b' predictions and the widths of the unresolved lines seem also to conform to case b' expectations.

If, the electronic angular momentum becomes completely uncoupled from the electric axis, the molecule conforms to Hund's case d'.[3] The same argument as advanced above holds, so that the structure may be considered to be that of a singlet state. The energy of a case d' state in a magnetic field can be easily calculated in a manner similar to that used in deriving relation (1). This leads to the expression[6]

$$\Delta E_{\text{mag}} = \frac{\mu_1 H M}{2K(K+1)}[K(K+1) + L(L+1) - R(R+1)] \tag{2}$$

where R is the nuclear rotation quantum number, L the orbital angular momentum quantum number (l for the present case), and K is the quantized resultant of L and R.

In general the magnetic energies of the two above cases are considerably different, the case d' energy being usually greater than that of case b'. Obviously, therefore, the Zeeman effect should afford a method of determining the degree of conformity to the two cases. Since complete uncoupling is not expected to occur at any critical value of n, K, or l-λ, many levels will correspond to cases intermediate between case b' and case d'. Hence the width of the Zeeman patterns should indicate, at least qualitatively, the degree of uncoupling. Harvey[8] has reported the qualitative effect of a magnetic field upon the orthohelium band lines involving levels of the $nd\delta$,$^3\Delta$; $nd\pi$,$^3\Pi$; $nd\sigma$,$^3\Sigma$ types. The extreme broadening of these lines led him to conclude that there is evidence of uncoupling in all of these levels.

Inasmuch as the Zeeman patterns of all but the first lines of the various branches of a band consist of a large number of components, a great number of them appear unresolved even at high dispersion. However, intensity re-

[5] F. Hund, Zeits. f. Physik **36,** 657 (1926).

[6] Cf. appendix for derivation of this and relation (2) given below.

[7] W. E. Curtis and W. Jevons, Proc. Roy. Soc. **A120,** 110 (1928).

[8] A. Harvey, Proc. Roy. Soc. **A126** ,583 (1930).

lations aid in comparing predicted overall widths with observations. Hönl[9] and Kronig[10] have given formulas which predict the relative intensities I, of the components of a spectral line in a magnetic field. These formulas apply equally well to case b' and case d' and may be stated as follows:

For Q branches,

$$M' = M'' + 1, \quad I = (\tfrac{1}{4})(K' - M' + 1)(K' + M')$$
$$M' = M'', \quad I = M'^2$$
$$M' = M'' - 1, \quad I = (\tfrac{1}{4})(K' - M')(K' + M' + 1)$$

For R branches,

$$M' = M'' + 1, \quad I = (\tfrac{1}{4})(K' + M' - 1)(K' + M')$$
$$M' = M'', \quad I = K'^2 - M'^2$$
$$M' = M'' - 1, \quad I = (\tfrac{1}{4})(K' - M' - 1)(K' - M')$$

For P branches,

$$M' = M'' + 1, \quad I = (\tfrac{1}{4})(K' - M' + 1)(K' - M' + 2)$$
$$M' = M'', \quad I = (K' + 1)^2 - M'^2$$
$$M' = M'' - 1, \quad I = (\tfrac{1}{4})(K' + M' + 1)(K' + M' + 2)$$

To check the predictions described above in a more quantitative manner than has been done by previous investigators, a fairly extensive investigation of the Zeeman effect in the ortho-helium bands under high dispersion was carried out.

Experimental Procedure

The helium discharge tube used in this investigation was of a special form designed by Mr. L. E. Pinney and fully described by Mulliken and Monk.[4] It consists of a Pyrex tube shaped to fit in the pole gap of a water-cooled magnet. The bands were excited by a small current from the secondary of a $\frac{1}{2}$ K.V.A. transformer with the usual spark gap in series. With a pressure of approximately 3 cm of helium in the tube the bands appeared with fair intensity. The discharge took place between the overlapping tips of a pair of aluminum electrodes placed normal to the magnetic field. The total discharge was confined to the center of the field and thus all radiation came from a uniform field. With the tubes used, giving a pole gap of about 6 mm, and a current of 12 amperes in the field windings, fields of from 28,000 to 30,500 gauss were obtained. The field strength of each plate was determined from the splitting of the atomic helium lines which were conveniently present.

The spectrum was photographed in the second and third orders of a twenty-one foot concave grating in a Rowland mounting, which gave a dispersion of 1.31A per mm in the second order. A large Nicol prism was placed in front of the spectrograph slit so that on all photographs only one polarization

[9] H. Hönl, Zeits. f. Physik **31**, 340 (1926).
[10] R. De L. Kronig, Zeits. f. Physik **31**, 885 (1926).

appeared. With the system used, the spectrum was of very low intensity so that exposures of from three to five days were necessary. An iron comparison spectrum was used on each plate.

Comparison of Experiment with Theory

The observed results are given in detail in the central column of the appended table. Tabulated on each side of the observations are the predicted results for case b' and for case d'. The component of each line which according to theory should appear with the maximum intensity is underlined. All of the separations are in terms of $\Delta\nu_{\text{normal}}$[11], i.e., half the width of the normal atomic triplet. The vast majority of the lines become, in the magnetic field, very diffuse so that comparator measurements of the overall widths of Zeeman patterns are not very reliable. However, microphotometer traces of the band lines indicate the degree of reliability of the various measurements. In the table the following notation has been used- *s* for singlet, *d* for doublet, *t* for triplet, *q* for quartet, (i.e., lines for which microphotometer traces indicate 1, 2, 3, or 4 maxima) and *b* for broad, for which traces give a wide maximum of fairly steep sides so that an overall width may be determined. Obviously the measurements marked *d*, *t*, or *q* are fairly reliable while those marked *b* are considerably less so.

Portions of typical bands are shown diagrammatically in Fig. 1 and 3. The predicted patterns have been drawn to scale both as to separation and relative intensity for each polarization. The photometer traces of the individual lines have been cut out and pasted on the diagrams between the predicted patterns. The scale of the traces varies, not only with the wave-length, but also for lines of nearly the same wave-length, since traces of both second and third order photographs were used. Since the traces have been used without enlargement or reduction, the scales of the predicted and observed patterns in the figures are often quite different, those of the predicted patterns being usually greater. This should be borne in mind when one examines the figures. The numbers below each predicted and observed pattern, however, expresses the indicated widths in terms of $\Delta\nu_{\text{normal}}$. In some cases the trace was not of sufficient density to photograph well so that it has been inked over. The trace of the line $Q(3)$ of $3d\sigma,{}^3\Sigma^{(0)}\rightarrow 2p\pi,{}^3\Pi^{(0)}$ in perpendicular polarization has been partially reconstructed since it is slightly overlapped by another line.

The comparison of prediction and observation can be made quite easily from an inspection of the figures and the table, but a brief account of its results will be given.

In the Q branch of the band $3p\pi,{}^3\Pi^{(0)}\rightarrow 2s\sigma,{}^3\Sigma^{(0)}$ nothing can be deduced concerning the conformity to the limiting cases b' and d', since the predicted patterns are identical. The agreement, however, with these predictions is obviously good. The measurements on the R branch of this band agree reasonably well with case b' predictions. The doublet structure decreases in width for increasing values of K in perpendicular polarization. The parallel

[11] $\Delta\nu_{\text{normal}}$ on the plates obtained corresponded at a wave-length of 4471A to a separation of 0.392 mm or 2.415 cm^{-1} for a field of 30,000 gauss.

polarization measurements in this branch also check well with case b' expectations. The excellent agreement for the line $R(1)$ as indicated in Fig. 1 is

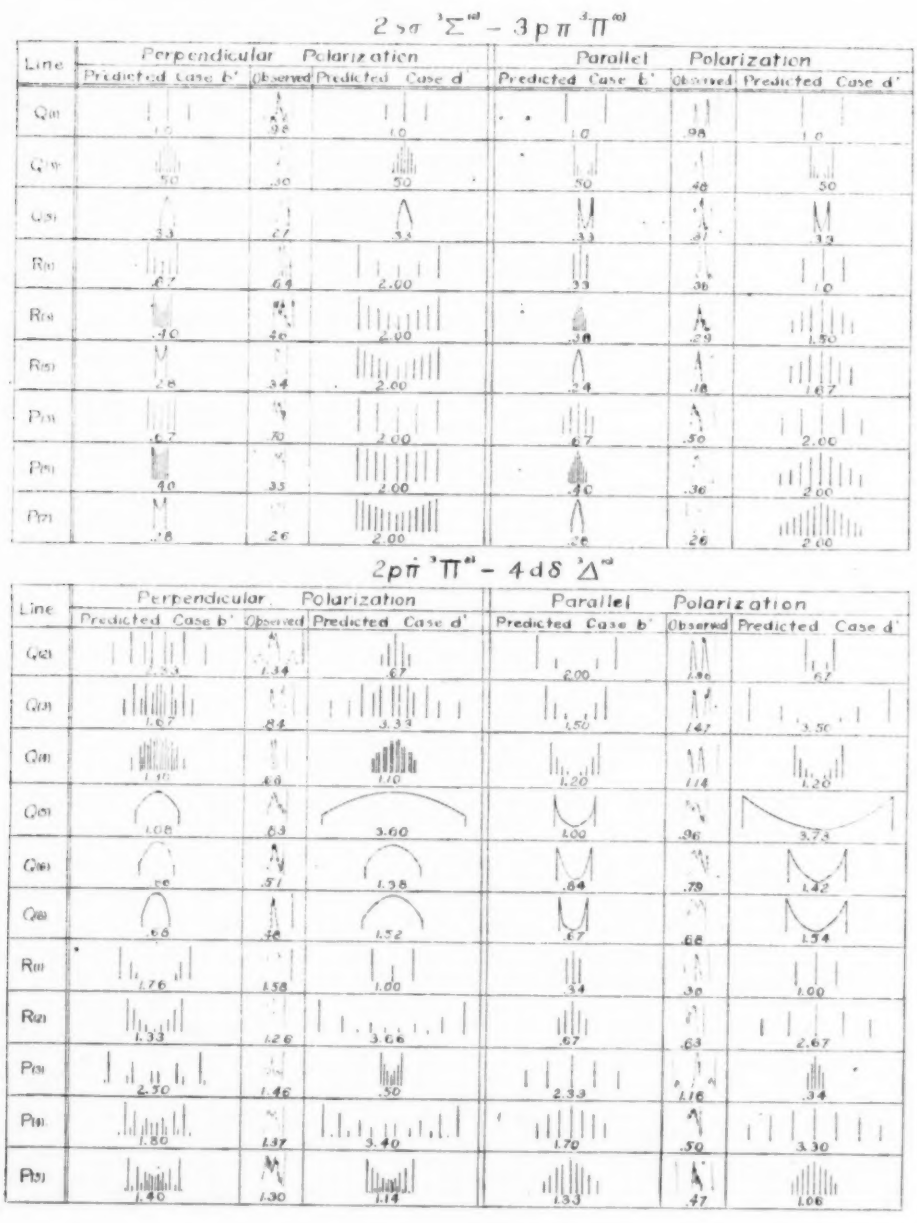

Fig. 1. Comparison of predicted Zeeman patterns and microphotometer traces of observed lines in bands in which there is little or no evidence of uncoupling phenomena The scale of the observed patterns is not uniform and is not the same as that of the predicted patterns.

of interest. The P branch also follows case b' predictions, although no resolved patterns were obtained.

The band $4p\pi,{}^3\Pi^{(0)} \rightarrow 2s\sigma,{}^3\Sigma^{(0)}$ gives patterns almost identical with those appearing in the corresponding lines in the band just discussed. The line $Q(9)$ is however anomalous. Curtis and Jevons[7] have described this line as a doublet of separation 6.6 cm^{-1} on zero-field plates. They further report that both components appear very broad in a magnetic field, the short-wave component ($\lambda = 3681.29$) being made so broad and diffuse as to nearly disappear. Although the band has not been observed without field by the author, it has been measured at field strengths of 5,000 gauss, and of 30,400 gauss in both polarizations. On all three plates it appears as a distinct and asymmetrical triplet with the long-wave and short-wave components separated from the central component by 1.61 cm^{-1} and 5.80 cm^{-1} respectively. This corresponds to a separation between the short-wave component and the center of gravity of the two long-wave components of 6.61 cm^{-1}. The three components are of

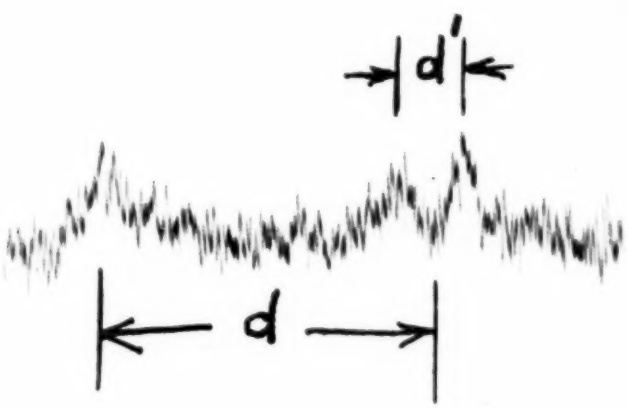

Fig. 2. Microphotometer trace of the anomalous line $Q(9)$ of $4p\pi,{}^3\Pi^{(0)} - 2s\sigma,{}^3\Sigma^{(0)}$ in a magnetic field of 30,400 gauss. The perpendicular polarization is here reproduced but the trace in parallel polarization is very nearly identical. $d = 6.61$ cm^{-1}, $d' = 1.61$ cm^{-1}.

about equal intensity. On the high field plates all of these lines are considerably broadened, the width decreasing for the three components with increasing wave-length. The widths observed are about the same as those expected for the $Q(9)$ line if it were single. The observed structure is apparently identical with that observed by Curtis and Jevons for the line $Q(9)$ in the 1,1 band. A probable interpretation of this structure is that a perturbation here occurs which causes the molecule to behave as in case b or case a instead of as in case b'. The line is no doubt a triplet both with and without field, corresponding to $K = 9$, $J = 8$, 9, and 10.[12] The microphotometer trace of this line is reproduced in Fig. 2.

The lines $Q(9)$ of the 0,1 and 1,1 bands of the same system look like doublets but are so faint that no measurements could be made, while the micro-

[12] Cf. G. H. Dieke, Nature, March 23, 1929 and R. S. Mulliken and G. S. Monk, Phys. Rev. **34,** 1532 (1929).

photometer traces are complicated by large plate grain. This is in agreement with the observations of Curtis and Jevons, save that no splitting has been bound in the long-wave component of the line in the 1,1 band, possibly due to the extreme faintness. This band system also shows perturbations in the lines $R(5)$ and $P(7)$. No resolved patterns appear, but both of these lines in the 0,0 band are wider on the author's plates than their neighbors, i.e., $R(3)$, $R(7)$ and $P(5)$, $P(9)$ respectively.

The band $4s\sigma,^3\Sigma^{(0)} \rightarrow 2p\pi,^3\Pi^{(0)}$ exhibits Zeeman effects in close agreement with case b' predictions. The agreements for the three bands so far discussed are in accordance with the reports of previous investigators. It is, therefore, safe to conclude that there is very little uncoupling of the orbital angular momentum in the $np\pi\ ^3\Pi$ levels. Since the level $2p\pi,\ ^3\Pi$ is the final state in all other bands studied here, it has been assumed that any uncoupling phenomenon which may occur must be a property of the initial state only.

In the band $4d\delta,^3\Delta^{(0)} \rightarrow 2p\pi,^3\Pi^{(0)}$ predictions for both case b' and case d' give very large patterns for small rotational energies. It is therefore dangerous to draw conclusions from unresolved patterns. However, inspection of Fig. 1 does reveal that the lines $Q(2)$, $R(1)$, $R(2)$, $P(3)$, $P(4)$, $P(5)$ in the perpendicular polarization and $Q(2)$, $Q(3)$, $Q(5)$, $Q(6)$, $Q(8)$, and $P(3)$ in the parallel polarization give evidence in favor of case b' coupling for the values of K involved. For large values of K a departure from case b' appears in the lines $Q(10)$, $P(9)$, $Q(14)$, and $P(11)$. However in none of these does the pattern conform at all closely to a case d' prediction. The failure to observe weak components which should appear at the edge of several lines in this band and others is probably due to the large grain of the rapid plates used. Microphotometer traces of such components are completely masked by the variations in density due to this grain. The evidence furnished by the band $3d\delta$, $^3\Delta^{(0)} \rightarrow 2p\pi,^3\Pi^{(0)}$ is identical. Conformity to case b' for low values of rotational energy is shown as above, but no lines involving large values of K were observed so that departure from this case is not shown. One may conclude that, in the levels $4d\delta,^3\Delta$ and $3d\delta,^3\Delta$, coupling of the orbital angular momentum of the excited electron to the electric axis is strong for all values of K less than nine and becomes weakened for large values of the rotation, though this uncoupling proceeds slowly. It should be pointed out that this is not in perfect agreement with the conclusions of Harvey[8] for these states. He concluded that the great width of lines in the field corresponding to small K values was indicative of uncoupling. A brief inspection of Figure 1 shows that case b' predictions are wider than case d' predictions for very small rotational energies. It is obvious, therefore, that great width of pattern alone is not indicative of the presence of uncoupling phenomona.

In the band $4d\pi,^3\Pi^{(0)} \rightarrow 2p\pi,^3\Pi^{(0)}$ the evidence of uncoupling occurs at much smaller rotational energies than in the last cases discussed above. The level $K=2$ is very apparently a case b' state as shown in the resolved patterns of the lines $Q(2)$ and $P(3)$ illustrated in Fig. 3. But for all values of K greater than two, there is departure from case b' predictions which increases with K so that for the line $R(15)$ the width of the pattern approaches fairly closely

the width of the case d' prediction. Similar evidence is offered by the band $3d\pi,{}^3\Pi^{(0)} \rightarrow 2p\pi,{}^3\Pi^{(0)}$. However it should be noted that the departure from

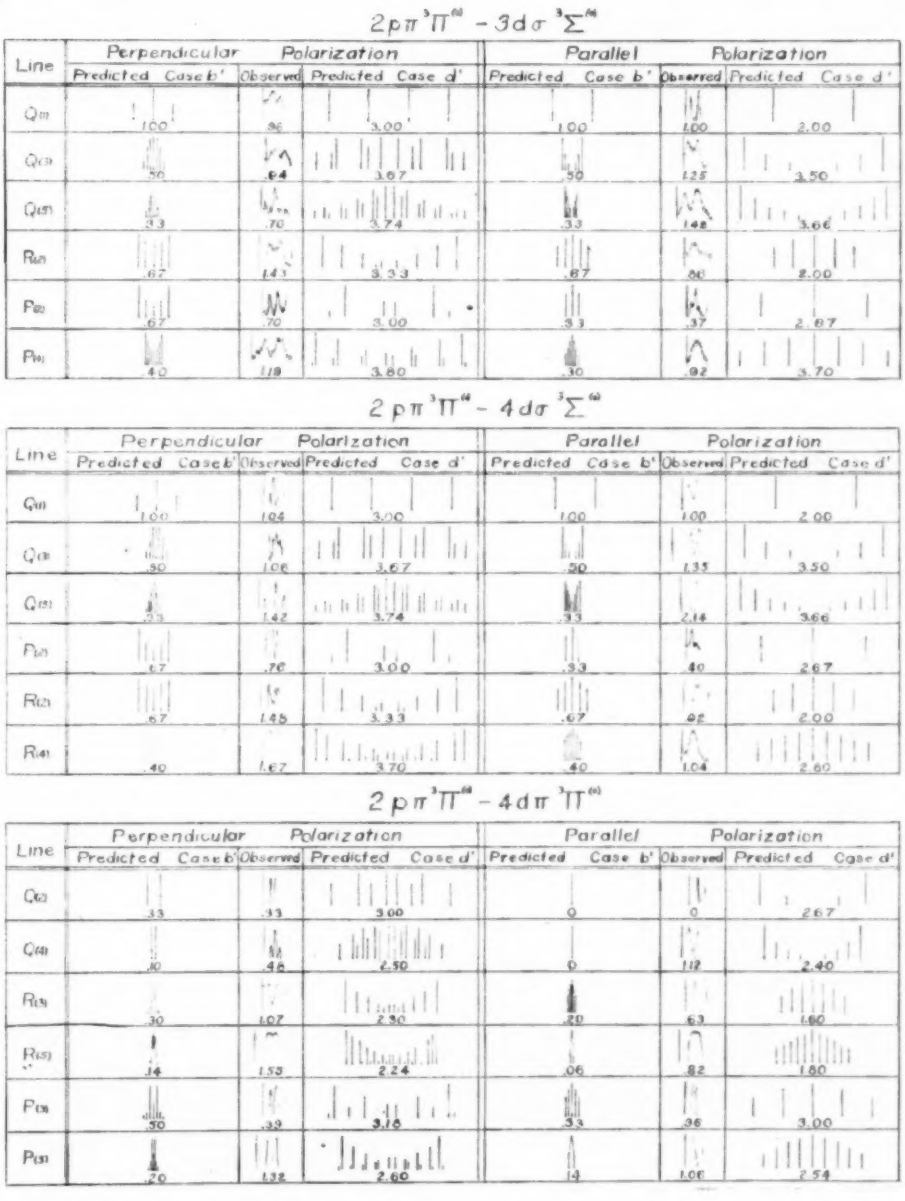
$2p\pi\,{}^3\Pi^{(0)} - 3d\sigma\,{}^3\Sigma^{(0)}$
Line
Perpendicular Polarization
Predicted Case b'
Observed
Predicted Case d'
Parallel Polarization
Predicted Case b'
Observed
Predicted Case d'
$Q_{(1)}$ 1.00 .86 3.00 1.00 1.00 2.00
$Q_{(2)}$ .50 .64 3.67 .50 1.25 3.50
$Q_{(3)}$ .33 .70 3.74 .33 1.48 3.66
$R_{(2)}$ .67 1.43 3.33 .67 .80 2.00
$P_{(2)}$ .67 .70 3.00 .33 .37 2.67
$P_{(1)}$ 4.0 1.19 3.80 .30 .92 3.70
$2p\pi\,{}^3\Pi^{(0)} - 4d\sigma\,{}^3\Sigma^{(0)}$
Line
Perpendicular Polarization
Predicted Case b'
Observed
Predicted Case d'
Parallel Polarization
Predicted Case b'
Observed
Predicted Case d'
$Q_{(1)}$ 1.00 1.04 3.00 1.00 1.00 2.00
$Q_{(2)}$ .50 1.06 3.67 .20 1.35 3.50
$Q_{(3)}$ .33 1.42 3.74 .33 2.14 3.66
$P_{(2)}$ .67 .70 3.00 .33 .40 2.67
$R_{(2)}$ .67 1.45 3.33 .67 .82 2.00
$R_{(1)}$ .40 1.67 3.70 .40 1.04 2.60
$2p\pi\,{}^3\Pi^{(0)} - 4d\pi\,{}^3\Pi^{(0)}$
Line
Perpendicular Polarization
Predicted Case b'
Observed
Predicted Case d'
Parallel Polarization
Predicted Case b'
Observed
Predicted Case d'
$Q_{(2)}$ .33 .33 3.00 0 0 2.67
$Q_{(3)}$ .30 .46 2.50 0 1.12 2.40
$R_{(3)}$ .30 1.07 2.30 .20 .63 1.60
$R_{(5)}$ .14 1.53 2.24 .06 .82 1.60
$P_{(3)}$ .50 .39 3.16 .33 .36 3.00
$P_{(5)}$ .20 1.32 2.60 .14 1.08 2.54

Fig. 3. Comparison of predicted and observed Zeeman patterns in bands which exhibit considerable evidence of uncoupling phenomena. The scales of the observed and predicted patterns are not the same.

case b' is less for the lines of this band than for the corresponding members of the band involving $4d\pi,{}^3\Pi$.

The uncoupling phenomenon appears for small values of K also in the band $3d\sigma,^3\Sigma^{(0)}\rightarrow 2p\pi,^3\Pi^{(0)}$. For $K=1$, the agreement between observation and case b' predictions is excellent as is evident in Fig. 3 for the resolved patterns of the lines $Q(1)$ and $P(2)$. But for all larger values of K the observations depart from case b' and this departure increases rapidly with increasing K. The

Fig. 4. Magnetic field energy level patterns for some states exhibiting uncoupling phenomena.

rate of departure is more rapid than for the bands involving $nd\pi,^3\Pi$ levels. The band $4d\sigma,^3\Sigma^{(0)}\rightarrow 2p\pi,^3\Pi^{(0)}$ furnishes exactly similar evidence. The patterns for this band are slightly wider than those of corresponding lines in $3d\sigma,^3\Sigma^{(0)}\rightarrow 2p\pi,^3\Pi^{(0)}$, indicating more rapid uncoupling, as can be easily seen in Fig. 3.

TABLE I.

The following notation has been used to describe the observed results: s, singlet; d, doublet, t, triplet; q, quartet; b, broad. All separations of components in resolved patterns and widths of unresolved patterns are expressed in terms of $\Delta\nu_{\text{normal}}$. This corresponds at $\lambda=4471$, to a separation of 0.392 mm or 2.415 cm^{-1} for a field of 30,000 gauss. The component of the predicted patterns which is expected to appear with maximum intensity is overscored.

Line	Predicted, Case b'	Observed		Predicted, Case d'
	$3p\pi,{}^3\Pi^{(0)}\rightarrow 2s\sigma,{}^3\Sigma^{(0)}$ ($\lambda=4675$)			
$Q(1)$	(σ) $\pm.50,\bar{0}$	t	$\pm.49,0$	$\pm.50,\bar{0}$
	(π) $\pm.50$	d	.98	$\pm.50$
$Q(3)$	(σ) $\pm.25,.17,.08,\bar{0}$	b	.30	$\pm.25,.17,.08,\bar{0}$
	(π) $\pm.\bar{25},.17,.08$	d	.48	$\pm.\bar{25},.17,.08$
$Q(5)$	(σ) $\pm.17,.13,.10,.07,.03,\bar{0}$	b	.27	$\pm.17,.13,.10,.07,.03,\bar{0}$
	(π) $\pm.\bar{17},.13,.10,.07,.03$	d	.31	$\pm.\bar{17},.13,.10,.07,.03$
$Q(7)$	(σ) overall .25	b	.25	overall .25
	(π) overall .25	d	.20	overall .25
$Q(9)$	(π) overall .20	d	.20	overall .20
$Q(11)$	(π) overall .17	d	.16	overall .17
$R(1)$	(σ) $\pm.\bar{33},.17,0$	d	.64	$\pm\bar{1}.\bar{00},.50,0$
	(π) $\pm.17,\bar{0}$	t	$\pm.16,0$	$\pm.50,\bar{0}$
$R(3)$	(σ) $\pm.\bar{20},.15,.10,.05,0$	d	.46	$\pm\bar{1}.\bar{00},.75,.50,.25,0$
	(π) $\pm.15,.10,.05,\bar{0}$	b	.29	$\pm.75,.50,.25,\bar{0}$
$R(5)$	(σ) overall .28	d	.34	overall 2.00
	(π) overall .24	b	.18	overall 1.67
$R(7)$	(σ) overall .22	d	.21	overall 2.00
	(π) overall .19	b	.16	overall 1.75
$R(9)$	(σ) overall .18	d	.17	overall 2.00
	(π) overall .16	s		overall 1.80
$P(3)$	(σ) $\pm.33,.17,0$	d	.70	$\pm\bar{1}.\bar{00},.50,0$
	(π) $\pm.33,.17,\bar{0}$	b	.50	$\pm1.00,.50,\bar{0}$
$P(5)$	(σ) $\pm.\bar{20},.15,.10,.05,0$	d	.35	$\pm\bar{1}.\bar{00},.75,.50,.25,0$
	(π) $\pm.20,.15,.10,.05,\bar{0}$	b	.36	$\pm1.00,.75,.50,.25,\bar{0}$
$P(7)$	(σ) overall .25	d	.26	overall 2.00
	(π) overall .25	b	.26	overall 2.00
	$4p\pi,{}^3\Pi^{(0)}\rightarrow 2s\sigma,{}^3\Sigma^{(0)}$ ($\lambda=3676$)			
$Q(1)$	(σ) $\pm.50,\bar{0}$	t	$\pm.50,0$	$\pm.50,\bar{0}$
	(π) $\pm.50$	d	1.07	$\pm.\bar{50}$
$Q(3)$	(σ) $\pm.25,.17,.08,\bar{0}$	b	.31	$\pm.25,.17,.08,\bar{0}$
	(π) $\pm.\bar{25},.17,.08$	d	.51	$\pm.25,.17,.08$
$Q(5)$	(σ) $\pm.17,.13,.10,.07,.03,0$	b	.26	$\pm.17,.13,.10,.07,.03,0$
	(π) $\pm.\bar{17},.13,.10,.07,.03$	d	.33	$\pm.\bar{17},.13,.10,.07,.03$
$Q(7)$	(σ) overall .25	b	.23	overall .25
	(π) overall .25	d	.27	overall .25
$Q(9)$	(σ) overall .20	*		overall .20
	(π) overall .20	*		overall .20

* This line is apparently a triplet both with or without field. The three components are all broadened in the field having a width of approximately .20 in both polarizations. See text for full description and discussion.

TABLE I. (*Continued*)

Line	Predicted, Case b'	Observed		Predicted, Case d'
$R(1)$	(σ) $\pm .\overline{33}, .17, 0$	d	.67	$\pm\overline{1}.\overline{00}, .50, 0$
$R(3)$	(σ) $\pm .\overline{20}, .15, .10, .05, 0$	d	.39	$\pm\overline{1}.\overline{00}, .75, .50, .25, 0$
$R(5)$	(σ) overall .29	d	.41	overall 2.00
$R(7)$	(σ) overall .22	d	.25	overall 2.00
	(π) overall .19	s		overall 1.80
$R(9)$	(σ) overall .18	d	.23	overall 2.00
	(π) overall .16	s		overall 1.80
$P(3)$	(σ) $\pm .\overline{33}, .17, 0$	d	.65	$\pm\overline{1}.\overline{00}, .50, 0$
$P(5)$	(σ) $\pm .\overline{20}, .15, .10, .05, \overline{0}$	d	.66	$\pm\overline{1}.\overline{00}, .75, .50, .25, \overline{0}$
$P(7)$	(σ) overall .29	d	.28	overall 2.00
	$4s\sigma, {}^3\Sigma^{(0)} \rightarrow 2p\pi, {}^3\Pi^{(0)}$ ($\lambda = 4545$)			
$Q(1)$	(σ) $\pm .50, \overline{0}$	t	$\pm .49, 0$	
	(π) $\pm .\overline{50}$	d	.96	
$Q(3)$	(σ) $\pm .25, .17, .08, \overline{0}$	b	.54	
$Q(5)$	(σ) overall .33	b	.31	
	(π) overall .33	d	.31	
$P(2)$	(σ) $\pm .\overline{33}, .17, 0$	d	.59	
$P(4)$	(σ) $\pm .20, .15, .10, .05, 0$	d	.39	
$P(6)$	(σ) overall .28	b	.27	
$P(8)$	(σ) overall .22	b	.21	
	$4d\delta, {}^3\Delta^{(0)} \rightarrow 2p\pi, {}^3\Pi^{(0)}$ ($\lambda = 4403$)			
$Q(2)$	(σ) $\pm 1.17, .\overline{67}, .33, .\overline{17}$	q	$\pm .67, .17$	$\pm .33, .17, \overline{0}$
	(π) $\pm\overline{1}.\overline{00}, .50$	d	1.96	$\pm .\overline{33}, .17$
$Q(3)$	(σ) $\pm .83, .42, .59, .\overline{33}, .17, .\overline{08}$	d	.84	$\pm 1.67, 1.25, 1.08, .67, .\overline{50}, .08$
	(π) $\pm .\overline{75}, .50, .25$	d	1.47	$\pm\overline{1}.\overline{75}, 1.17, .68$
$Q(5)$	(σ) $\pm .54, .44, .37, .33, .27, .23, .17, .\overline{13}, .07, .\overline{03}$	b	.83	$\pm 1.80, 1.50, 1.43, 1.13, 1.07, .77, .70, .40, .\overline{33}, .\overline{03}$
	(π) $\pm .\overline{50}, .40, .20, .10$	d	.96	$\pm\overline{1}.\overline{86}, 1.45, 1.40, .73, .37$
$Q(6)$	(σ) overall .90	b	.48	overall 1.36
	(π) overall .86	d	.79	overall 1.43
$Q(8)$	(σ) overall .68	b	.48	overall 1.52
	(π) overall .66	d	.68	overall 1.55
$Q(10)$	(σ) overall .56	b	.96	overall 1.62
	(π) overall .54	d	1.05	overall 1.63
$Q(14)$	(σ) overall .47	b	.98	overall 2.34
$R(1)$	(σ) $\pm .\overline{83}, .67, .50$	d	1.58	$\pm .\overline{50}, 0$
	(π) $\pm .17, \overline{0}$	b	.30	$\pm .50, \overline{0}$

TABLE I. (*Continued*).

Line	Predicted, Case b'	Observed	Predicted, Case d'
$R(2)$	(σ) $\pm.\overline{67}, .50, .33, .17, 0$	d 1.26	$\pm\overline{1}.\overline{83}, 1.17, .83, .50, .17$
$P(3)$	(σ) $\pm\overline{1}.\overline{25}, 1.08, .67, .50, .08$	t $\pm.73, 0$	$\pm.\overline{25}, .17, .08, 0$
	(π) $\pm.85, .57, .28, \overline{0}$	t $\pm.58, 0$	$\pm.17, .08, \overline{0}$
$P(4)$	(σ) $\pm.\overline{90}, .80, .62, .52, .33, .23, .05$	b 1.37	$\pm\overline{1}.\overline{70}, 1.60, 1.15, 1.05, .60, .50, .05$
	(π) $\pm.85, .57, .28, \overline{0}$	t $\pm.25, 0$	$\pm1.65, 1.10, .55, \overline{0}$
$P(5)$	(σ) $\pm.\overline{70}, .63, .53, .47, .37, .30, .20, .13, .03$	d 1.30	$\pm.\overline{57}, .50, .43, .37, .30, .23, .17, .10, .03$
	(π) $\pm.67, .50, .33, .17, \overline{0}$	b .47	$\pm.53, .40, .27, .13, \overline{0}$
$P(7)$	(σ) overall .97	d 1.01	overall 1.32
$P(9)$	(σ) overall .73	d .87	overall 1.53
$P(11)$	(σ) overall .56	d .69	overall 1.65
	$3d\delta, {}^3\Delta^{(0)} \rightarrow 2p\pi, {}^3\Pi^{(0)}$ ($\lambda = 5733$)		
$Q(2)$	(σ) $\pm1.17, .\overline{67}, .33, .\overline{17}$	q $\pm.70, .19$	$\pm.33, .17, \overline{0}$
	(π) $\pm\overline{1}.\overline{00}, 50$	d 1.90	$\pm.\overline{33}, .17$
$Q(3)$	(σ) $\pm.83, .59, .42, .\overline{33}, .17, .\overline{08}$	d .89	$\pm1.67, 1.25, 1.08, .67, .\overline{50}, .\overline{08}$
$Q(4)$	(σ) $\pm.65, .50, .40, .35, .25, .\overline{20}, .10, .\overline{05}$	d .60	$\pm.55, .50, .45, .40, .25, .20, .\overline{10}, .\overline{05}$
	(π) $\pm.\overline{60}, .45, .30, .15$	d .93	$\pm.\overline{60}, .45, .30, .15$
$Q(5)$	(σ) $\pm.54, .44, .37\ .33\ .27, .23, .17, .\overline{13}, .07, .\overline{03}$	d .77	$\pm1.80, 1.50, 1.43, 1.13, 1.07, .77, .70, .40, .\overline{33}, .03$
$R(1)$	(σ) $\pm.\overline{83}, .67, .50$	d 1.32	$\pm.\overline{50}, 0$
$R(2)$	(σ) $\pm.\overline{67}, .50, .33, .17, 0$	d .84	$\pm\overline{1}.\overline{83}, 1.17, .83, .50, .17$
$P(4)$	(π) $\pm.85, .57, .28, \overline{0}$	d .61	$\pm1.65, 1.10, .55, 0$
	$4d\pi, {}^3\Pi^{(0)} \rightarrow 2p\pi, {}^3\Pi^{(0)}$ ($\lambda = 4440$)		
$Q(2)$	(σ) $\pm.\overline{17}$	d .33	$\pm1.50, .\overline{83}, .50, .17$
	(π) $\overline{0}$	s	$\pm\overline{1}.\overline{33}, .67$
$Q(4)$	(σ) $\pm.\overline{05}$	t $\pm.24, 0$	$\pm1.25, .95, .85, .65, .\overline{35}, .25, .\overline{05}$
	(π) $\overline{0}$	d 1.12	$\pm\overline{1}.\overline{20}, .90, .60, .30$
$Q(10)$	(σ) overall .02	b .37	overall 2.36
$Q(12)$	(π) overall .01	d 1.22	overall 2.26
$R(3)$	(σ) $\pm.15, .12, .08, .\overline{03}, .02$	d 1.07	$\pm\overline{1}.\overline{15}, .88, .62, .45, .35, .18, .08$
	(π) $\pm.10, .07, .03, \overline{0}$	b .63	$\pm.80, .53, .27, \overline{0}$
$R(5)$	(σ) $\pm.07, .06, .05, .\overline{03}, .02, .01, .00$	d 1.55	$\pm\overline{1}.\overline{12}, .94, .76, .69, .57, .51, .40, .33, .21, .14, .03$
	(π) $\pm.03, .02, .01, 0$	b .82	$\pm.90, .73, .54, .36, 1.8, .\overline{0}$

TABLE I. (*Continued*)

Line	Predicted, Case *b'*		Observed		Predicted, Case *d'*
$R(11)$	(σ) overall .03		d	1.61	overall 2.13
	(π) overall .02		b	1.63	overall 1.92
$R(15)$	(σ) overall .02		d	1.70	overall 2.09
$R(15)$	(σ) overall .02		d	1.77	overall 2.07
$P(3)$	(σ) $\pm$.25, .17, .$\overline{08}$, 0		d	.39	$\pm$1.59, $\overline{1}$.$\overline{42}$, .83, .66, .08
	(π) $\pm$.17, .08, $\bar{0}$		b	.36	$\pm$1.50, .75, 0
$P(5)$	(σ) $\pm$.08, .05, .$\overline{03}$, .02		d	1.32	$\pm$1.30, $\overline{1}$.$\overline{23}$, .98, .92, .67, .60, .35, .28, .03
	(π) $\pm$.07, .05, .$\overline{03}$, .02, 0		b	1.06	$\pm$1.27, .95, .63, .32, $\bar{0}$
$P(7)$	(σ) overall .07		t	$\pm$1.04, 0	overall 2.34
	(π) overall .07		b	1.22	overall 2.30
$P(9)$	(σ) overall .04		t	$\pm$.75, 0	overall 2.18
		$3d\pi,{}^3\Pi^{(0)}\rightarrow 2p\pi,{}^3\Pi^{(0)}$ (λ=5887)			
$Q(2)$	(σ) $\pm$.$\overline{17}$		d	.32	$\pm$1.50, .$\overline{83}$, .50, .17
	(π) 0		s		$\pm\overline{1}$.$\overline{33}$, .67
$Q(4)$	(σ) $\pm$.$\overline{05}$		b	.47	$\pm$1.25, .95, .85, .65, .$\overline{35}$, .25, .$\overline{05}$
	(π) 0		d	.98	$\pm\overline{1}$.20, .90, .60, .30
$R(3)$	(σ) $\pm$.15, .12, .08, .$\overline{05}$, .02		d	.99	$\pm\overline{1}$.$\overline{15}$, .88, .62, .45, .35, .18, .08
	(π) $\pm$.10, .07, .03, $\bar{0}$		b	.62	$\pm$.80, .53, .27, $\bar{0}$
$R(5)$	(σ) $\pm$.07, .06, .05, .03, .02, .02, .$\overline{01}$, 0		d	1.39	$\pm\overline{1}$.$\overline{12}$, .94, .76, .69, .57, .51, .40, .33, .21, .14, .03
	(π) $\pm$.03, .02, .01, $\bar{0}$		b	.79	$\pm$.90, .73, .54, .36, .18, $\bar{0}$
$P(3)$	(σ) $\pm$.25, .17, .$\overline{08}$, 0		d	.36	$\pm$.159, $\overline{1}$.$\overline{42}$, .83, .66, .08
	(π) $\pm$.17, .08, $\bar{0}$		b	.34	$\pm$1.50, .75, $\bar{0}$
		$3d\sigma,{}^3\Sigma^{(0)}\rightarrow 2p\pi,{}^3\Pi^{(0)}$ (λ=5954)			
$Q(1)$	(σ) $\pm$.50, $\bar{0}$		t	$\pm$.47, 0	$\pm$1.50, .$\overline{50}$
	(π) $\pm$.50		d	1.00	$\pm\overline{1}$.$\overline{00}$
$Q(3)$	(σ) $\pm$.25, .17, .$\overline{08}$, 0		t	$\pm$.47, 0	$\pm$1.83, 1.25, 1.08, .$\overline{67}$, .50, .08
	(π) $\pm$.$\overline{25}$, .17, .08		d	1.25	$\pm\overline{1}$.$\overline{76}$, 1.17, .59
$Q(5)$	(σ) $\pm$.17, .13, .10, .$\overline{07}$, .03, 0		t	$\pm$.35, 0	$\pm$1.87, 1.50, 1.43, 1.13, .77, .70, .$\overline{40}$, .33, .$\overline{03}$
	(π) $\pm$.$\overline{17}$, .13, .10, .07, .03		d	1.48	$\pm\overline{1}$.$\overline{83}$, 1.47, 1.10, .73, .37
$Q(7)$	(σ) overall .25		t	$\pm$.31, 0	overall 3.78
	(π) overall .25		d	1.84	overall 3.50
$Q(9)$	(π) overall .20		d	2.10	ovrall 3.80
$Q(13)$	(σ) overall		t	$\pm$.28, 0	overall 3.86
$P(2)$	(σ) $\pm$.33, .17, 0		d	.70	$\pm$1.50, $\overline{1}$.$\overline{17}$, .17
	(π) $\pm$.17, $\bar{0}$		b	.37	$\pm$1.33, $\bar{0}$

TABLE I. (*Continued*)

Line	Predicsted, Case b'	Observed	Predicated, Case d'
$P(4)$	(σ) $\pm .\overline{20}, .15, .10, .05, \bar{0}$	d 1.19	$\pm 1.90, \bar{1}.\overline{80}, 1.28, 1.18, .67, .57, .05$
	(π) $\pm .15, .10, .05, \bar{0}$	b .92	$\pm 1.85, 1.23, .62, \bar{0}$
$R(2)$	(σ) $.\overline{33}, .17, 0$	d 1.43	$\pm \bar{1}.\overline{67}, 1.17, .67, .33, .17$
	(π) $\pm .\overline{33}, .17, \bar{0}$	b .86	$\pm 1.00, .50, \bar{0}$
$R(4)$	(σ) $\pm .\overline{20}, .15, .10, .05, 0$	d 1.42	$\pm \bar{1}.\overline{85}, 1.45, 1.10, 1.00, .75, .65, .40, .30, .05$
	$4d\sigma,^3\Sigma^{(0)} \rightarrow 2p\pi,^3\Pi^{(0)}$ ($\lambda = 4458$)		
$Q(1)$	(σ) $\pm .50, \bar{0}$	t $\pm .52, 0$	$\pm \bar{1}.\overline{50}, .50$
	(π) $\pm .\overline{50}$	d 1.00	$\pm \bar{1}.\overline{00}$
$Q(3)$	(σ) $\pm .25, .17, .\overline{08}, 0$	t $\pm .53, 0$	$\pm 1.83, 1.25, 1.08, .\overline{67}, .50, .\overline{08}$
	(π) $\pm .\overline{25}, .17, .08$	d 1.35	$\bar{1}.\overline{75}, 1.17, .59$
$Q(5)$	(σ) $\pm .\bar{1}\overline{7}, .13, .10, .\overline{07}. .03, 0$	t $\pm .71, 0$	$\pm 1.87, 1.50, 1.43, 1.13, .77, .70, .\overline{40}, .33, .\overline{03}$
	(π) $\pm .\bar{1}\overline{7}, .13, .10, .07, .03$	d 2.14	$\pm \bar{1}.\overline{83}, 1.47, 1.10, .73, .37$
$R(2)$	(σ) $\pm .\overline{33}, .17, 0$	d 1.48	$\pm \bar{1}.\overline{67}, 1.17, .67, .33, .17$
	(π) $\pm .33, .17, \bar{0}$	b .92	$\pm 1.00, .50, \bar{0}$
$R(4)$	(σ) $\pm .\overline{20}, .15, .10, .05, 0$	d 1.67	$\pm \bar{1}.\overline{85}, 1.45, 1.10, 1.00 .75, .65, .40, .30, .05$
	(π) $\pm .20, .15, .10, .05, \bar{0}$	b 1.04	$\pm 1.40, 1.05, .70, .35, \bar{0}$
$R(8)$	(σ) overall .22	d 1.67	overall 3.78
	(π) overall .22	b 1.13	overall 3.33
$R(10)$	(σ) overall .18	d 1.86	overall 3.82
	(π) overall .18	b 1.21	overall 3.45
$P(2)$	(σ) $\pm .\overline{33}, .17, 0$	d .76	$\pm 1.50, \bar{1}.\bar{1}\overline{7}, .17$
	(π) $\pm .17, \bar{0}$	b .40	$\pm 1.33, \bar{0}$
	$4d\sigma,^3\Sigma^{(1)} \rightarrow 2p\pi,^3\Pi^{(1)}$ ($\lambda = 4479$)		
$Q(1)$	(π) $\pm .\overline{50}$	d 1.03	$\pm \bar{1}.\overline{00}$
$Q(3)$	(π) $\pm .\overline{25}, .17, .\overline{08}$	d 1.35	$\pm \bar{1}.\overline{75}, 1.17, .59$
$Q(5)$	(π) $\pm .\bar{1}\overline{7}, .13, .10, .07, .03$	d 2.12	$\pm \bar{1}.\overline{83}, 1.47, 1.10, .73, .37$
$Q(7)$	(π) overall .25	d 2.06	overall 3.50

As a summary of these observational results, Fig. 4 has been prepared to show at least qualitatively the magnetic field energy level patterns for some of those states in which uncoupling has been observed. The magnetic splitting of the $2p\pi,^3\Pi$ level has been assumed to follow case b' rigorously, as pointed out above. This made it possible to at least estimate, or in the case of resolved patterns, to determine definitely the energy of the levels of $4d\delta,^3\Delta$; $4d\pi,^3\Pi$; $4d\sigma,^3\Sigma$; and $3d\sigma,^3\Sigma$ in a magnetic field, wherever there were several observations involving the same rotational level. The numbers beside the levels or groups of levels are widths or separations in terms of $\Delta\nu_{\text{normal}}$.

SUMMARY

In summary, it may be said that Zeeman patterns in the ortho-helium bands involving levels of the $d\delta,^3\Delta$; $d\pi,^3\Pi$; and $d\sigma,^3\Sigma$ types have beenf ound to agree with theoretical predictions. The Zeeman effect in these levels offers a means of following the phenomenon of the uncoupling of the orbital angular momentum of the excited electron from the electric axis predicted and observed by previous investigators.

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APPENDIX

Derivation of formulas (1) and (2) appearing in text

(1) *Energy of the case b' singlet state in a magnetic field.* In terms of the vector model,[3] the vector representing the angular momentum of the excited electron, $l^*h/2\pi$, is thought of as being so rigidly bound to the molecular axis that the projection of l^* on this axis is a true quantum number, λ, corresponding to an angular momentum $\lambda h/2\pi$. This vector precesses with that representing the nuclear rotation, $Oh/2\pi$ (not a quantum number) about their quantized resultant $K^*h/2\pi$. If then this molecule is placed in a magnetic field of strength H, K^* will process about H and a magnetic energy will appear. This energy is written by Hund[8] as

$$\Delta E_{\text{mag}} = \overline{\mu_1 \underline{\lambda} \cdot \underline{H}}.$$

The average value of the scalar product of the vectors λ and H is obtained by finding the average contribution of λ to K^* and then the average value of the quantized projection of K^* on the direction of H (i.e., the magnetic quantum number M). Resolving λ into components perpendicular and parallel to K^*, it is easily seen that the average value of the perpendicular component is zero while the contribution of the parallel component is $\lambda \cos(\lambda, K^*)$. The projection of this quantity on the direction of H is, $\lambda \cos(\lambda, K^*) \cos(K^*, H)$. Hence

$$\Delta E_{\text{mag}} = \mu_1 H \lambda \cos(H, K^*) \cos(\lambda, K^*).$$

Now

$$\cos(H, K^*) = M/K^*, \quad \cos(\lambda, K^*) = \lambda/K^*,$$
$$K^{*2} = K(K+1).$$

Hence

$$\Delta E_{\text{mag}} = \mu_1 H M \lambda^2 / K(K+1). \tag{1}$$

(2) *Energy of a case d' singlet state in a magnetic field.* In terms of the vector model, the orbital angular momentum of the excited electron, $l^*h/2\pi$, is thought of as being totally uncoupled from the molecular axis. The vector representing this angular momentum and that representing the rotational

energy of the nuclei, $R^*h/2\pi$, precess about their quantized resultant K^*. The energy of the molecule in a magnetic field may be then calculated very much as above.

$$\Delta E_{\text{mag}} = \mu_1 \underline{\overline{l^*}} \cdot \underline{H}$$

$$l_{\parallel}^* = l^* \cos (l^*, K^*)$$

$$\Delta E_{\text{mag}} = \mu_1 H l^* \cos (l^*, K^*) \cos (K^*, H)$$

$$\cos (l^*, K^*) = \frac{l^{*2} + K^{*2} - R^{*2}}{2l^*K^*}$$

$$\cos (K^*, H) = M/K^*$$

$$K^{*2} = K(K+1), \quad l^{*2} = l(l+1), \quad R^{*2} = R(R+1)$$

$$\Delta E_{\text{mag}} = \frac{\mu_1 H M}{2K(K+1)} [K(K-1) + l(l+1) - R(R+1)]. \qquad (2)$$

THE M-SERIES ABSORPTION SPECTRUM OF TANTALUM

By Charles A. Whitmer
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(Received August 3, 1931)

Abstract

The M-series absorption spectrum of tantalum (73) has been investigated, with a vacuum spectrograph of the Siegbahn type. The absorption screens were metallic tantalum, prepared by an evaporation process. Spectrograms were obtained for three absorption limits at 5.64A (M_{III}), 6.773A (M_{IV}), and 6.997A (M_V). When the experimental ν/R values are compared to values calculated from L-absorption and emission data, the experimental values for M_{IV} and M_V show a displacement toward higher frequencies and the M_{III} limit a displacement toward lower frequencies. These discrepancies are in agreement with those found by several other investigators in the region from W(74) to Au(79). The M_{III} limit has the appearance of a white line, and M_{IV} and M_V are diffuse in character. The possibility of an explanation of these discrepancies on the basis of transitions to levels in the periphery of the atom is suggested.

Introduction

THE measurements of the M-absorption limits of the heavier elements are of particular interest, not only because of the contribution of additional information on the values of the energy levels, but also because the experimental values obtained for the M_{II}, M_{III}, M_{IV}, and M_V edges from Au(79) to W(74) do not agree within experimental error with the values calculated from L-emission and absorption data. The discrepancy in M_{IV} and M_V was first noted by Zumstein in this laboratory.[1] Zumstein measured all five of the M-limits of tungsten. Following Zumstein, Rogers[2] investigated the M-absorption of platinum, iridium, and osmium. Johnson[3] repeated Roger's measurements on platinum, using the pure metal as absorber, and in addition measured M_I, M_{III}, M_{IV} and M_V of gold. In addition to the above work, which has been done in this laboratory, an article by E. Lindberg[4] reported measurements on the M_{III}, M_{IV} and M_V edges of Ur, Th, Bi, Pb, Tl, Hg, Au, Pt, and W.

The results of these investigators show that in the case of M_{IV} and M_V for all the elements from Au(79) to W(74), the experimentally determined wavelengths are systematically shorter than the corresponding calculated values, while for the M_{II} and M_{III} limits the experimentally determined wavelengths are longer than the calculated values.* The experimental wave-

[1] R. V. Zumstein, Phys. Rev. **25**, 747 (1925).
[2] R. A. Rogers, Phys. Rev. **30**, 747 (1927).
[3] A. J. M. Johnson, Phys. Rev. **34**, 1106 (1929).
[4] E. Lindberg, Zeits. f. Physik **54**, 632 (1929).

* The calculated values referred to here are taken from the International Critical Tables Vol. VI, p. 35. They are evidently computed from the following relations:

$M_I = L_{III} - L_l$ $\quad M_{IV} = L_{II} - L\beta_1$
$M_I = L_{II} - L\eta$ $\quad M_{IV} = L_{III} - L\alpha_2$
$M_{II} = L_I - L\beta_4$ $\quad M_V = L_{III} - L\alpha_1$
$M_{III} = L_I - L\beta_3$

lengths for M_{I} are all slightly shorter than the corresponding calculated values, although the discrepancy for this limit is of the order of the experimental error.

An adequate theory has not been developed to explain these discrepancies. Johnson[3] concluded from his work with metallic gold and platinum that the cause of the shift of values, at least for these elements, did not lie in the chemical state of the absorbing material.

The purpose of this research was to extend these investigations to an additional element whose atomic number is less than that of tungsten. Tantalum was chosen because it can be obtained in a chemically pure and uncombined state, thus enabling a check to be made on the effect of chemical combination. Moreover, the experimental difficulties in working in long wave-length regions made it desirable to choose an element whose atomic number was as large as possible. Finally, the fact that tantalum can be obtained either in a thin foil or in wire form suggested the possibility of preparing absorption screens directly from the foil, or from the wire by an evaporation process.

Apparatus and Experimental Procedure

The Siegbahn type vacuum spectrograph used in this investigation has been described by both Zumstein[1] and Rogers.[2] It was altered in only a few minor details. The mercury vapor from the diffusion pump and occluded vapors from the walls of the metal tube were removed from the tube by a liquid air trap. The removal of the vapors decreased the sputtering of the filament markedly, and rendered the occurrence of gaseous discharges less likely, so that a steady operation of the tube could be had at 100 milliamperes over long periods of time.

The crystal used was gypsum. Imperial Eclipse dry plates manufactured by the Imperial Dry Plate Co., Cricklewood, London, produced spectrograms of excellent contrast. The time of exposure ranged from 10 to 40 hours. Tube voltages ranged from 2000 to 5000 volts; the tube voltage was kept low enough at all times to prevent masking of the absorption limits by second order general radiation. In order to obtain spectrograms of the M_{IV} and M_{V} edges it was necessary to substitute for the usual tungsten filament one of molybdenum, for the sputtered tungsten on the target produced the relatively intense W$M\alpha$ and W$M\beta$ emission lines, which masked the M_{V} and M_{IV} limits respectively. Although the W$M\alpha$ line appeared faintly on some of the spectrograms, it was weak enough not to mask the M_{V} edge, and was thus useful as a reference line. The operation of the molybdenum filament was quite satisfactory, although it did not last nearly as long as the tungsten filament.

An attempt was made to prepare absorption screens by thinning tantalum foil with hydrofluoric acid, but a screen of sufficient thinness could not be obtained. The screens used were prepared by evaporating the tantalum from an incandescent filament in a high vacuum. The evaporated metal was deposited on a base prepared by blowing large bubbles of soft sodium glass, from which a flat piece free from strain can be selected. The thickness of the glass based used was of the order of 10^{-4} centimeters, and transmitted approximately 75 percent of the incident radiation.

The evaporator was similar to that used by Johnson. It consisted of a bell-jar, evacuated by a two-stage mercury diffusion pump. In the bell-jar two filaments in parallel were supported horizontally two centimeters above a table which supported the glass base on which the tantalum was deposited. At first this table was water cooled, but it was found that the water-cooled surface on one side and the hot filament on the other created strains in the glass which caused it to shatter. The best table was found to be of sheet iron set loosely on the water-cooled bell-jar base. Enough cooling was obtained by conduction to keep the glass from melting, yet without causing it to warp. After the deposition of the metal the screen was cemented to a metal frame. The same screens were used for all the limits measured; the thinner screens produced more distinct spectrograms for the M_{IV} and M_V edges. Screens of sufficient thickness were obtained in from one to two hours of evaporation; it is estimated that their thickness ranged from 10^{-4} to 10^{-5} centimeters.

The measurement of the wave-length of the edges was accomplished by reference to several known emission lines.* It can be shown by a Taylor's expansion of Bragg's law that, to a second approximation,

$$\Delta\lambda = \frac{d}{\gamma}\left(\cos\theta - \frac{\Delta s}{4}\sin\theta\right)\Delta s, \tag{1}$$

where d is the grating constant of the crystal, r the radius of the focal circle, θ the angle between the crystal face and the incident beam, and Δs the distance between the known emission line and the absorption limit. Δs was measured with a low-powered traveling microscope, and the corresponding $\Delta\lambda$ calculated from (1). θ is obtained from Bragg's law, using the wave-length value of the known emission line. The advantage of this method of interpolation lies in the fact that it is accurate over the entire length of the spectrogram, a distance of about two centimeters.

Tests of formula (1) on identified emission lines gave results accurate within 0.003A. The chief error in this method of measurement arises in setting the cross-hairs of the microscope on the diffuse absorption limits. The average error in this setting was less than 0.015 centimeters, which corresponds to approximately 0.007A. The total error has been estimated to be not greater than ± 0.010A.

Results

Spectrograms were obtained for the M_{III}, M_{IV}, and M_V limits of tantalum. The mean value of the measurements on the individual plates are tabulated in Table I, and these values are averaged to give the final mean value for the absorption limit. In Table II are listed the wave-lengths of the lines used for reference in accordance with the method of interpolation described above.

* In addition, the sharp K-absorption edge of Si, from the absorption in the glass base, which appeared on the spectrograms of Ta M_{IV} and M_V, was very convenient for reference. The wave-length of this edge was taken from a paper by G. B. Deodhar, Nature, May 24, 1930.

TABLE I. *Tantalum M-series absorption.*

Limit	Screen number	Plate number	Reference lines	Wave-length	Mean wave-length	Mean ν/R
M_{III}	17	177	Pb$M\alpha$, Au$M\alpha$, Au$M\beta$	5.648A		
M_{III}	19	181	Pb$M\alpha$	5.643		
M_{III}	17	182	Pt$M\alpha$, Pb$M\alpha$, Pt$M\beta$ Mo$L\alpha$, Mo$L\beta$	5.651		
M_{III}	22	183	Pt$M\alpha$, Pb$M\alpha$, Pt$M\beta$ Mo$L\alpha$, Mo$L\beta$	5.646		
M_{III}	18	185	Pt$M\alpha$, Pb$M\alpha$, Pt$M\beta$	5.643	5.647A	161.35
M_{IV}	17	190	Si K-absorption limit, Si$K\alpha$	6.768		
M_{IV}	17	191	Si K-absorption limit, Si$K\alpha$	6.766		
M_{IV}	17	192	Si K-absorption limit, Si$K\alpha$	6.769		
M_{IV}	23	199	Si K-absorption limit, Si$K\alpha$, W$M\alpha$, Sn$L\beta$	6.777		
M_{IV}	17	202	W$M\alpha$, Sn$L\beta$	6.781		
M_{IV}	17	203	Si K-absorption limit, Si$K\alpha$	6.775	6.773	134.54
M_V	17	190	Si K-absorption limit, Si$K\alpha$	6.992		
M_V	17	191	Si K-absorption limit, Si$K\alpha$	6.994		
M_V	17	192	Si K-absorption limit, Si$K\alpha$, W$M\alpha$	6.998		
M_V	23	199	Si K-absorption limit, Si$K\alpha$, Sn$L\alpha$, W$M\alpha$, Sn$L\beta$	6.994		
M_V	17	202	Si K-absorption limit, Si$K\alpha$	7.003		
M_V	17	203	Si K-absorption limit, Si$K\alpha$	6.997	6.997	130.24

TABLE II. *Wave-lengths of reference lines.*

Sn$L\alpha$	7.184	(second order)	Au$M\alpha$	5.827
Si$K\alpha$	7.109		Pt$M\beta$	5.820
W$M\alpha$	6.973		Au$M\beta$	5.611
Sn$L\beta$	6.756	(second order)	Mo$L\alpha$	5.394
SiK-abs.	6.705		Pb$M\alpha$	5.273
Pt$M\alpha$	6.041		Mo$L\beta$	5.166

DISCUSSION

The M_{II} edge of tantalum was masked by the K-absorption of the sulphur in the gypsum crystal and consequently was not observed. Attempts at obtaining the M_I edge were unsuccessful, due, in all probability, to the fact that this edge is least intense of the M-limits and consequently requires a screen with a thickness very near the optimum in order to be detected. That there is an optimum thickness has been shown by Sandström,[5] who has derived for it the expression

$$d = \frac{\log \mu_2 - \log \mu_1}{\mu_2 - \mu_1},$$

where μ_1 and μ_2 are the absorption coefficients on the long and short wave-length sides of an absorption limit respectively.

The M_{III} edge had the appearance of a single white line, the short wave-length side being very nearly, if not quite, as sharp as the long wave-length

[5] A. Sandström, Zeits. f. Physik **65**, 632 (1930).

side. Such a white line absorption was also observed by Rogers[2] for the M_{I}, M_{II}, and M_{III} limits of Os(76), Ir(77), and Pt(78). Johnson[3] did not observe such a white line structure for Pt M_{I} and M_{III}, and Lindberg[4] makes no mention of it in his article.

The M_{IV} and M_{V} limits were of the true edge type, and were rather diffuse in character.

Table III shows the discrepancy between the observed and calculated values of tantalum.* A comparison of the calculated values of the M-limits with the experimental values for the region between Bi(83) and Yb(70),

TABLE III. *A comparison of the computed and experimental values of the M-limits of tantalum.*

Limit	λ, exp.	λ, cal.	Δλ	ν/R, exp.	ν/R, cal.	$\Delta\nu/R$
M_{III}	5.647A	5.594A	+0.053A	161.35	162.9	−1.55
M_{IV}	6.773	6.893	−0.120	134.54	132.2	+2.34
M_{V}	6.997	7.130	−0.133	130.24	127.8	+2.44

$\Delta\lambda = \lambda$ (exp.) $-\lambda$(cal.) $\qquad \Delta\nu/R = \nu/R$ (exp.) $-\nu/R$ (cal.)

* See the footnote above regarding the method of calculation.

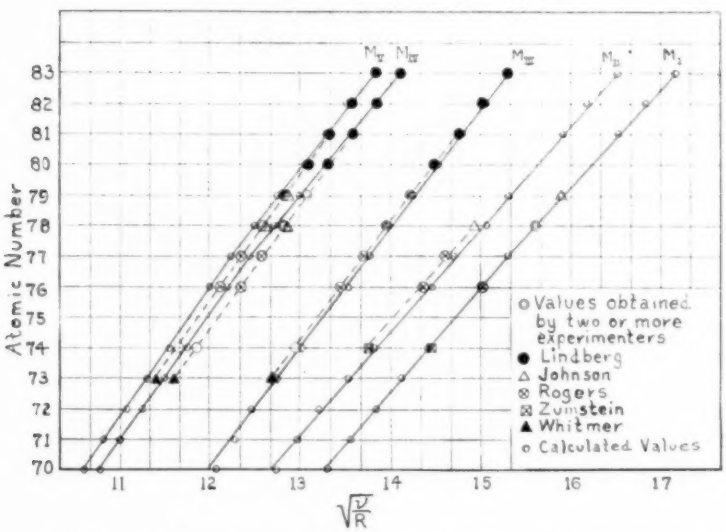

Fig. 1. Values of $(\nu/R)^{\frac{1}{2}}$ plotted against atomic number. Full lines represent values given in the International Critical Tables.

which have been measured by the various experimenters, is shown graphically in Fig. 1, in which $(\nu/R)^{1/2}$ has been plotted against atomic number. The calculated values are taken from the International Critical Tables;** a careful check of the calculations show that they are calculated from experimentally determined L-limits and L-emission lines.

** The computed values for Os(76) and Ir(77) are not given in the International Critical Tables. The values used are taken from an article by Cork, Phys. Rev. **21**, 326 (1923).

The calculated values of $(\nu/R)^{1/2}$ for M_{I}, M_{IV} and M_{V} show a change of slope of the curve at Ir(77), which is not evident in the experimental values for M_{IV} and M_{V}; in the case of M_{I} the experimental points are apparently in good agreement with the calculated curve.

The experimental evidence at hand indicates two possibilities for an explanation of the discrepancies shown in Fig. 1. The observed limit may not correspond to the energy necessary to remove an M electron to infinity. For example, the simultaneous ejection of an M electron and an outer electron by a single quantum would result in a shift of the limit to higher energy levels. Or, the absorbed quantum may remove the M electron to one of the outer permitted levels of the atom.[6] Such an absorption would produce white lines, shifted to lower frequencies than the calculated values, such as has been reported for M_{II} and M_{III} by Rogers, and for Ta M_{III} by the writer. Thus the experimental evidence indicates the possibility of an explanation of the discrepancies shown in Fig. 1 by means of transitions to permitted levels in the periphery of the atom.

In conclusion, the writer wishes to express his appreciation to the staff of the Department of Physics of the State University of Iowa for their interest and assistance, and in particular to Professor G. W. Stewart, who suggested and directed this investigation.

[6] This suggestion, recently made by Siegbahn, Zeits. f. Physik **67**, 567 (1931) has just come to the attention of the author.

THE BAND SPECTRUM OF BENZENE: EXISTENCE OF A SMALL VIBRATIONAL FREQUENCY IN THE NORMAL STATE[1]

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(Received August 3, 1931)

Abstract

A vibrational frequency of 160 cm^{-1} in the band spectrum of benzene, postulated by Henri but called into question by Kronenberger and Pringsheim, is discussed from the point of view of the available spectral and Raman data but no definite conclusion as to its origin in the normal state of the molecule is reached. Experimental evidence is then brought forward to show that the observed intensity distribution of absorption bands having this separation corresponds closely to the distribution calculated from the Boltzmann law with the addition of certain reasonable assumptions, on the basis that the 160 cm^{-1} frequency occurs in the normal state. Further checks are obtained by repeating the measurements and calculations for higher temperatures. The possible origin of this small vibrational frequency in the benzene molecule is briefly discussed.

Introduction

NUMEROUS attempts have been made in recent years to analyze the known ultraviolet spectra of benzene—absorption, fluorescence and Tesla luminescence—in terms of the theory of band spectra[3–9] but thus far no completely satisfactory scheme has been presented. It is evident that, for a complex polyatomic molecule like benzene, a number of vibrational frequencies, corresponding to the numerous degrees of freedom, must be anticipated for each electronic state. The discovery of the Raman effect and its subsequent theoretical interpretation led to the hope that the characteristic frequencies thus uncovered and attributed to the normal state of the molecule, would yield the clue to the analysis of the electronic-vibration spectra of various complex molecules. However, even in the application of Raman data to the problem of the relatively simple infrared absorption spectra of the polyatomic molecules, conclusive results have not been obtained in all cases. Langer and Meggers,[10] after a careful determination of the Raman frequen-

[1] The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University.

[3] Henri, Jour. de Physique **3**, 181 (1922); Structure des Molecules, Paris (1925), p. 108.

[4] Pringsheim and Reimann, Zeits. f. Physik **29**, 115 (1924).

[5] Reimann, Ann. d. Physik **80**, 43 (1926).

[6] Kronenberger and Pringsheim, Zeits. f. Physik **40**, 75 (1927).

[7] Marsh, J. Chem. Soc. **123**, 3319 (1923); Phil. Mag. **49**, 1206 (1925).

[8] McVicker and Marsh, J. Chem. Soc. **123**, 642, 817 (1923).

[9] Austin and Black, Phys. Rev. **35**, 452 (1930).

[10] Langer and Meggers, B. of S. Jour. of Research **4**, 711 (1930).

cies for benzene and several other organic compounds, could find no exact correlation with the infrared absorption spectra of these compounds. In other instances it has been observed that certain of the Raman frequencies agree closely with vibrational frequencies deduced from a study of the infrared spectrum and, in a few cases, Raman lines have been associated with inactive frequencies, whose existence had already been surmised from infrared data by application of the combination principle.[11] The correspondence between the Raman frequencies and the vibrational frequencies deduced from the electronic-vibration bands of diatomic molecules is especially striking for H_2, O_2 and N_2.[12] Nevertheless, there remains, in the case of most organic molecules, a number of Raman lines, which cannot be interpreted as active or inactive frequencies, while their infrared spectra also exhibit bands, which have not been accounted for as harmonics or combinations of recognized fundamental frequencies.

In his analysis of the ultraviolet absorption spectrum of benzene, Henri[3] employed several vibrational frequencies, among them one of approximately 160 cm^{-1}, which has also been used by Marsh,[7] Reimann[5] and Austin and Black[9] in their interpretation of the emission spectra of benzene. Kronenberger and Pringsheim[6] have objected to this interpretation and have suggested an alternative energy level scheme in which a frequency of 80 cm^{-1} occurs as the difference between two large frequencies, approximately 1000 and 920 cm^{-1}, for the normal and electronically excited molecule respectively. They have themselves pointed out objections to this arrangement, among these the necessity of assuming the existence of large numbers of normal molecules in the cold vapor possessing eight or more quanta of vibrational energy (more than one volt). It must be noted further that the bands so interpreted by Kronenberger and Pringsheim do not have a separation of exactly 80 cm^{-1}, as they deduce from their data obtained under low dispersion, but that these separations are, in a typical case, 88, 72, 89, 71, 91, 69 cm^{-1}, as measured from plates obtained with a Hilger E_1 spectrograph having a dispersion of 3A per mm in the region under discussion. There is a definite alternation in these values far beyond the experimental error (± 1 cm^{-1}); furthermore, the sum of the numbers in successive pairs is accurately 160 cm^{-1}. In a more recent paper, Kronenberger[13] reverts to the use of the 160 cm^{-1} frequency difference but attributes it to a difference between two vibrational frequencies of the excited state ($924-772=152$ cm^{-1}). Aside from the lack of quantitative agreement with observations, this interpretation is certainly inadequate, since it accounts for but a single occurrence of this difference in a band group, whereas each strong band in the absorption and fluorescence spectrum is accompanied by as many as six subsidiary bands, each separated from its neighbor by 160 cm^{-1}.

The question then arises as to the origin of this small frequency difference. It does not occur among those found in the Raman spectrum of benzene,

[11] Schaeffer, Trans. Far. Soc. **25,** 841 (1929).
[12] McLennan, Trans. Far. Soc. **25,** 797 (1929).
[13] Kronenberger, Zeits. f. Physik **63,** 509 (1930).

nor can it be deduced from a combination of these frequencies, as is evident from a consideration of Langer and Megger's accurate data[10] in Table I.

TABLE I. *Raman frequencies of benzene* (cm^{-1})

605.7,	848.6,	992.1,	1177.3,	1585.2,	1604.5,	2946.9,	3045.4,	3060.1 (3185?)

The corresponding infrared wave-length, 62.5μ, lies in a region which has not been investigated for benzene, while the available infrared data, for the region of shorter wave-lengths, are not sufficiently accurate to allow a definite statement as to its occurrence in combination bands.[14]

It has therefore appeared worth while to attempt to secure experimental corroboration of the reasonable assumption that the 160 cm^{-1} frequency difference is due to one of the many possible, characteristic vibrations of the normal state of the molecule. Since the energy corresponding to this frequency (0.02 volt) is of the same order of magnitude as the average energy of thermal agitation at room temperature, benzene molecules possessing one or more quanta of this vibration may be expected to be present in appreciable quantities. The distribution can be computed by means of the Boltzmann function:

$$\frac{N_t}{N} = \frac{e^{-E_t/kT}}{\sum_t e^{-E_t/kT}} \tag{1}$$

where N = total number of molecules, N_t = number of molecules in state "t," E_t = energy of state "t" in ergs, k = Boltzmann's constant and T = absolute temperature. It is implicitly assumed in the derivation of this expression that the *a priori* probability is equal to unity for all the energy states.[15] If we now examine the absorption spectrum of benzene and consider the set of band heads corresponding to transitions between these several levels of the 160 cm^{-1} vibration of the normal electronic state and a single level of the excited molecule, the intensity distribution should be similar to the above Boltzmann distribution. This will hold strictly if the transition probability from each of these lower levels is the same. In terms of the Franck-Condon theory of intensity distribution in vibration bands,[16] equality for the transition probabilities may be anticipated because of the small energy difference between the lowest and the highest of the vibrational levels under consideration (0.1 volt). A further test of the validity of the above reasoning is obtained by examining the absorption spectrum at a series of temperatures, for each of which a new Boltzmann distribution is set up and hence a new intensity distribution. Qualitatively, the effect of higher temperatures is to favor the states of higher

[14] Brackett, Phys. Rev. **37,** 108 (1931) has recently reported the presence of satellites in one of the overtone bands of benzene (at 1.2μ), having separations of 162 cm^{-1}.

[15] This assumption is justified for the vibrational states of diatomic molecules by Birge, Mol. Spectra in Gases, Nat. Res. Council Bulletin, No. 57, p. 157 (1926) and has been found by D. M. Dennison (private communication) to hold for certain types of vibrations in polyatomic molecules.

[16] For references and discussion of the theory, see article by R. S. Mulliken, Rev. Mod. Phys. **2,** 79 (1930).

energy at the expense of those of lower energy: the intensity distribution will tend to become more nearly uniform as illustrated in Fig. 1.

Favorable conditions for the observance and measurement of this effect in benzene were found in the band group at 37,494 cm^{-1}. Extending toward lower wave numbers, as many as six members of the series with separations of 160 cm^{-1} can be observed at the higher temperatures (200–350°C); the only other absorption bands to appear with measurable intensity in this region, at the pressure and length of vapor path used, fall at positions intermediate between the above bands.

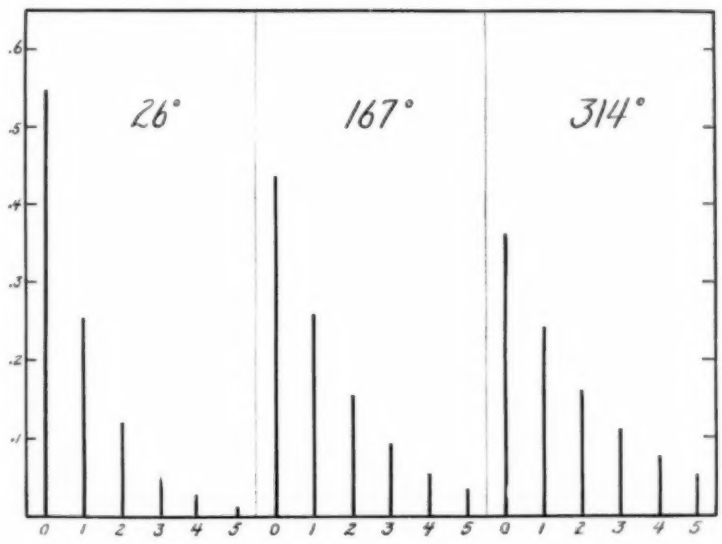

Fig. 1. Boltzmann distribution at several temperatures for energy levels having separations of 160 cm^{-1}.

Experimental Procedure

The benzene was prepared by dry distillation of chemically pure benzoic acid. After successive washings with sodium hydroxide, sulfuric acid and water and drying over $CaCl_2$, the product was carefully distilled, the first and last portions of the distillate being discarded. The benzene so obtained had a boiling point of 79°C at a barometric pressure of 740 mm of mercury.

A small weighed quantity was sealed in a thin-walled, capillary vial, which was placed in a quartz absorption tube, 4 cm long, having plane polished, sealed-on windows of quartz. After evacuation with a two-stage mercury diffusion pump, the absorption tube was sealed off and the vial, containing the benzene, was shattered by impact. The tube was placed in the center of a cylindrical electric furnace, 40 cm in length, whose ends were closed by quartz plates. The temperature was read from a thermometer, introduced into the furnace through a well directly above the absorption tube.

The absorption spectrum was photographed with a Hilger spectrograph, type C_1. The light source was a high-frequency Tesla discharge between

brass electrodes under water,[17] from the center of which discharge, when the electrodes are well separated (about 15 mm), a continuous spectrum is obtained, without any superposition of absorption or emission lines due to the material of the electrodes. This is highly desirable, since it makes possible a direct evaluation of intensities from the microphotometric records. In operation the source is quite constant, so that a series of exposures can be made under comparable conditions.

The amount of benzene introduced into the absorption tube was so chosen that it completely vaporized at room temperature, an essential condition, since it insures that the total number of molecules in the light path remains constant over the range of temperatures investigated (20°–350°C). For the

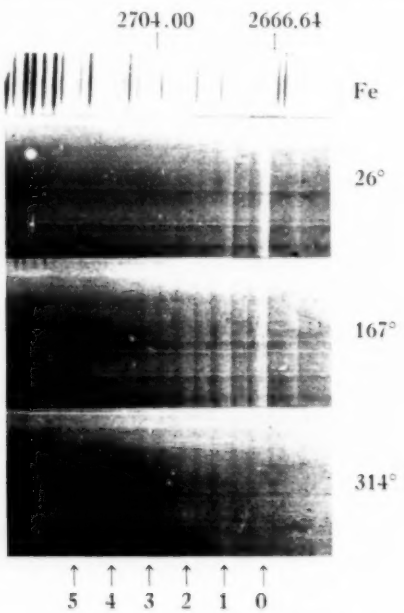

Fig. 2. Absorption spectrum of benzene vapor near the origin at 37, 494 cm^{-1} at several temperatures. The numbers are quantum designations of the 160 cm^{-1} vibrational bands.

final exposures, from which the data here reported were taken, a quantity much less than this limiting amount was used, so that the absorption of the strongest member of the series being studied was not more than 50 percent. The purpose of this precaution was to have sufficient blackening of the photographic plate in the center of each absorption line in order to be able to apply the law of blackening. This law is such that only after a certain minimum exposure, does the density, d, bear the functional relation to the incident light intensity:

$$d = \gamma \log It^p - k, \tag{2}$$

where γ = contrast factor, I = intensity, t = time, p = Schwarzschild's constant and k = inertia factor.

[17] Howe, Phys. Rev. **6**, 681 (1916).

Fig. 2 is a reproduction of a series of spectrograms at different temperatures. Arrows indicate the bands, whose separations are 160 cm^{-1}. The two predicted effects are readily observable: (1) the appearance of higher members of the series at the higher temperatures and (2) the relative decrease in intensity of the first member with respect to the succeeding ones at the higher temperatures. The quantitative analysis of the results was carried out on microphotometric records obtained from this and similar plates.

Evaluation of the Microphotometric Records

The problem is one of determining the extinction coefficient for each band, since that quantity is proportional to the concentration of the vapor:

$$\alpha_t = \beta c_t = 1/d \log I_0/I, \tag{3}$$

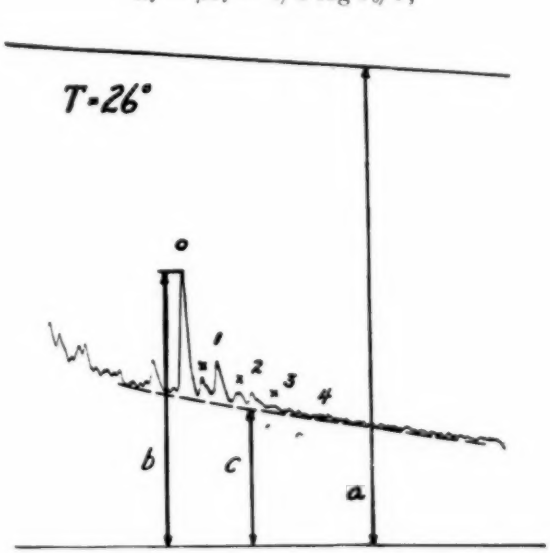

Fig. 3. Microphotometric record of absorption bands of benzene, showing intensity distribution among vibrational bands ($\omega = 160$ cm^{-1}) at 26°C. The lowest horizontal line gives the zero reading of the galvanometer, the uppermost one the reading through the clear portion of the photographic plate. The bands marked with an "x" are those having frequency separations of approximately 80 cm^{-1} from their neighbors (see text).

in which β = absorption coefficient, c_t = concentration in state t, and d = thickness. For this purpose, the following procedure was followed, which, while not absolutely rigorous, does give the proper order of magnitude. On each record were impressed the zero reading of the galvanometer and readings through the clear portion of the plate in the direct vicinity of the two ends of the portion of the spectrum studied. The galvanometer readings for the long wave-length portion of the spectrum, where no absorption occurred, were extrapolated, as shown in Fig. 3, through the region under investigation. This drawn line may then be regarded as the probable galvanometer reading, had there been no *selective* absorption. The following measurements were made for each band: the distance a, (see Fig. 3) from the zero line to the "clear"

line; the distance b, from the zero line to the peak of the absorption band and finally the distance c, from the zero line to the extrapolated line. Then

$$d_1 = \log a/b \text{ and } d_0 = \log a/c \tag{4}$$

where d_1 is the density of the photographic image at the center of the band and d_0 = the extrapolated density at the same point. But from Eq. (2) above:

$$d_1 = \gamma \log I_1 t^p - k;\ d_0 = \gamma \log I_0 t^p - k. \tag{5}$$

I_1 = transmitted intensity, I_0 = extrapolated incident intensity. t, p, k, and γ can be regarded as constants, since all such measurements were made at a given wave-length on a single spectrogram. Eq. (5) can therefore be rewritten as:

$$d_1 = \gamma \log I_1 + (\gamma p \log t - k);\ d_0 = \gamma \log I_0 + (\gamma p \log t - k) \tag{6}$$

Therefore:

$$d_0 - d_1 = \gamma \log I_0 - \gamma \log I_1 = \gamma \log I_0/I_1 \tag{7}$$

Eq. (7) is identical with (3), except for the multiplicative constant, so that $(d_0 - d_1)_t$ for a given band as computed from the microphotometric record is proportional to a_t and hence to the concentration of molecules in the initial state t, of the absorption process. The extrapolated line in the above treatment has in every case been drawn tangent to the troughs, i.e., to the points of minimum transmission through the plate. The absolute values for $(d_0 - d_1)_t$ are somewhat affected by the method of drawing this extrapolated line but we are only concerned with relative values and these remain comparatively unaffected under the present circumstances.

Discussion of Results

A typical set of data from one microphotometric record is presented in Table II. The symbols heading the first seven columns have been defined in the previous section. Since the values in column 7, $(d_0 - d_1)_t$, are proportional to the concentration of molecules in the corresponding states, the numbers obtained by dividing each of them by the sum of all these values are equivalent to the fractional populations of each state, (column 8). The last column gives the corresponding values calculated from the Boltzmann function.

Table II. *Typical measurements for T = 26° C.*

n''	a	b	c	d_1	d_0	$d_0 - d_1$	$\frac{d_0 - d_1}{\Sigma_n (d_0 - d_1)}$	Calc. Boltzmann distribution
0	93.6	53.9	32.0	0.239	0.466	0.227	0.545	0.547
1	93.2	38.4	30.2	0.385	0.490	0.105	0.250	0.254
2	92.8	32.0	28.9	0.462	0.507	0.045	0.109	0.119
3	92.4	29.1	27.5	0.502	0.526	0.024	0.058	0.055
4	92.0	27.2	26.2	0.529	0.545	0.016	0.038	0.026

Owing to imperfections on the spectrograms, instrumental errors and errors of measurement, the final results, tabulated in Table III, are averaged

from three or four microphotometric records, obtained from a single absorption spectrogram. The spectra for the several temperatures listed were photographed on a single plate and so subjected to similar conditions of developing, fixing, etc. As a final precaution, after the absorption spectrum at the highest temperature (314°C) had been photographed, the tube was allowed to cool to room temperature and the absorption again photographed: there was no evidence of change in the absorption spectrum of benzene as a result of holding the vapor at the above temperature for about two hours.

TABLE III. *Initial distribution of benzene molecules in states having* $\omega''=160$ *cm*$^{-1}$ *at various temperatures.*

	26°		167°		240°		314°	
n''	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	0.557	0.547	0.411	0.438	0.355	0.388	0.337	0.358
1	0.242	0.254	0.284	0.260	0.246	0.248	0.222	0.242
2	0.111	0.118	0.167	0.155	0.175	0.158	0.170	0.162
3	0.057	0.055	0.090	0.092	0.117	0.102	0.128	0.111
4	0.034	0.026	0.049	0.054	0.068	0.065	0.090	0.075
5	—	—	—	—	0.040	0.042	0.052	0.051

The agreement between the observed intensity distribution and the calculated Boltzmann distribution, not only at room temperature but up to double that on the absolute scale, is strong evidence in favor of the assumption that the frequency of 160 cm^{-1} corresponds to one of the possible modes of vibration of the normal state of the molecule. This result is therefore in definite disagreement with Pringsheim's suggestion that the true frequency differences in the benzene spectrum are 80 cm^{-1}.

In considering the origin of a vibrational frequency as small as 160 cm^{-1}, two possibilities arise: either (a) the restraining forces are weak, or (b) the separation of the atoms involved is large. The first condition is satisfied by the motion of a carbon atom in a direction perpendicular to the plane of the benzene ring. This involves a bending of the valence bonds of carbon to carbon, a case considered by Andrews[18] in his calculation of the specific heat of benzene at low temperatures. He interprets a postulated fundamental band in the infrared spectrum at 28μ[19] (= 357 cm^{-1}) as arising from this bending. In a study of mechanical models, simulating the various structures assigned to benzene by organic chemists, Kettering, Shutts and Andrews[20] have found a frequency corresponding to about 360 cm^{-1}, which they correlate with the above postulated infrared band and with a Raman line at this frequency, reported by them but which has not been recorded by any of the numerous investigators of the Raman effect in benzene.[21]

[18] Andrews, Chem. Reviews **5,** 533 (1928).

[19] Ellis, Phys. Rev. **27,** 298 (1926). Ellis has recently cast doubt on his previous interpretation of this band, Trans. Faraday Soc. **25,** 888 (1929).

[20] Kettering, Shutts and Andrews, Phys. Rev. **36,** 531 (1930).

[21] See Reference 6. Also Ganesan and Venkateswaran, Ind. J. of Phys. **4,** 223 (1929); Dabadghao, Ind. J. of Phys. **5,** 207 (1930); Bhagavantam, Ind. J. of Phys. **5,** 615 (1930).

The other alternative, a large separation of the atoms, can only be satisfied by considering diametrically opposite carbon atoms of the hexagonal "ring." Since the carbon atoms are firmly bound to each other, as evidenced by the high stability of the compound, a vibration between opposite carbon atoms must also produce stresses between neighboring carbon atoms and hence would involve relatively high frequencies (about 1000 cm^{-1}), as brought out in the above mentioned work on mechanical models. The second alternative appears therefore to be inapplicable in this case.

It would be interesting to see whether slight changes in the spring constants or in the method of coupling of the springs might not lead to the appearance of lower frequencies for the bending vibrations, while leaving those in the plane of the ring unchanged. Kettering and his coworkers have based their development of the mechanical model on the assumption that the Raman frequencies coincide with all the fundamental modes of vibration of the molecular system, while as pointed out in the introduction above, this is not necessarily true.

VIBRATIONAL QUANTUM ANALYSIS OF THE VISIBLE ABSORPTION BANDS OF BROMINE

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(Received August 7, 1931)

Abstract

The absorption bands of bromine from 5100A to 7600A are classified into two band systems having a common lower level. One of these includes nearly all of the previously recorded bands of bromine while the other comprises a group of relatively weak bands lying in the extreme red. The upper level of the extreme red system differs from that of the main system in that it dissociates into normal atoms. Measurements of the vibrational isotope effect are given for a number of bands in the main system leading to a revision of the quantum numbering and of the vibrational constants.

Introduction

IN THE vibrational analysis of the bromine bands by Kuhn,[1] which was carried out primarily for the purpose of obtaining the heat of dissociation, the isotope effect resulting from the existence of two isotopes of bromine, 78.93 and 80.93,[2] (atomic wt. 79.93) was not observed. The analysis did not include a large number of bands in the region 5300–5600A, and this omission lead to an inconsistent assignment of quantum numbers as Birge[3] discovered when recalculating the constants. Nakamura's[4] more numerous and more extensive measurements, when arranged in av', v'' matrix diagram show discordant G' and G'' differences. The present work was undertaken for the purpose of securing a more satisfactory vibrational analysis, utilizing, if possible, the isotope effect to obtain the true quantum numbering.

Experimental

Of photographs taken with a three prism Steinheil spectrograph, 10 and 21 ft. concave gratings, those taken in the first order of the 10 ft. grating (Paschen mounting; dispersion 5.4A/mm) were chosen as the best compromise between high dispersion and sharpness of band heads. With this dispersion the partial resolution of fine structure was quite troublesome but with the prism instrument the isotope shifts were hardly measureable and with the 21 ft. grating only those bands for which the isotope effect is negligibly small were distinct. Lines of the iron arc, second order where necessary, served as standards, and conversion from wave-lengths in air to wave numbers in vacuum was made by means of Kayser's "Tabelle der Schwingungzahlen." In general the measurements are not accurate to better than 2 cm^{-1}, and in cases where the isotope effect has not been identified the error is considerably greater.

[1] H. Kuhn, Zeits. f. Physik **39**, 77 (1926).
[2] F. W. Aston, Proc. Royal Society **115**, 487 (1927).
[3] R. T. Birge, International Critical Tables **V**, 411 (1929), and private communication.
[4] G. Nakamura, Mem. Coll. Sci. Kyoto Univ. **9**, 335 (1926).

Orthochromatic, panchromatic, and extreme red (kryptocyanine) plates were used to cover the visible and near infrared spectrum. Pyrex absorption tubes, from 10 cm to 4 m in length contained the bromine (Kahlbaum) at pressures determined by the temperature of attached bulbs. The absorbing vapor was at room temperature in all experiments except those designed to

TABLE I. *Frequencies of band heads in the main absorption system of bromine, in* cm^{-1}.

v'	$\tilde{\nu}'$	0	1	2	3	4	5	$\Delta G'_{v+\frac{1}{2}}$
4	0					15185.5		149.6
5	1					15335.1		144.1
6	2			16113.4	15796.4	15479.2	15169.2	143.2
7	3			16255.4	15938.6	15624.6	15311.6	138.8
8	4			16394.5	16078.4	15762.6	15450.0	135.8
9	5			16530.6	16214.0	15898.8	15585.5	129.8
10	6			16660.4	16343.4	16029.4	15714.7	128.7
11	7			16789.1	16472.2	16156.4	15845.1	122.6
12	8			16912.9	16594.4	16278.9	15967.2	122.1
13	9		17353.3	17033.7	16718.7	16401.4		114.8
14	10		17467.1	17150.0	16831.5	16517.5		110.9
15	11	17901.2	17579.1	17259.8				108.5
16	12	18009.1	17688.0	17368.4				104.0
17	·	18113.2	17792.1	17472.1				99.7
18	·	18213.4	17890.9	17572.0				96.7
19	·	18310.9	17988.1	17667.6				90.9
20	·	18401.6	18077.8	17759.9				87.8
21	·	18490.4	18166.5	17845.8				81.9
22	·		18248.4					80.0
23		18650.2	18328.4					76.1
24		18725.9	18405.0					71.0
25		18796.4	18477.5					67.3
26		18865.2	18543.3					65.6
27		18928.8	18610.9					61.3
28		18990.1						55.5
29		19045.6						49.1
30		19094.7						52.3
31		19147.0						45.9
32		19192.9						44.4
33		19237.5						40.3
34		19275.8						36.9
35		19312.7						31.8
36		19344.5						30.3
37		19374.8						28.6
38		19403.4						25.7
39		19429.1						20.7
40		19449.8						20.5
41		19470.3						15.9
42		19486.2						13.3
43		19499.5						13.0
44		19512.5						11.8
45		19524.3						7.2
46		19531.5						10.7
47		19542.2						9.2
48		19551.4						
$\Delta G''_{v+\frac{1}{2}}$		321.6	319.3	316.9	315.4	312.4		

intensify certain members of the extreme red system. For these experiments the 4 m tube, containing excess liquid bromine, was heated to 50°C, thereby increasing the vapor pressure to about 600 mm.

It is well known that the maximum intensity of absorption for bromine

occurs in the region of continuous absorption at about 4100A. This can be observed with a very small quantity of absorbing vapor. On increasing the pressure the spectrum develops progressively toward longer wave-lengths and at the same time the region of continuous absorption widens. With the highest pressure employed the extreme red system appears with good intensity while below 6400A absorption is complete. This constitutes the only evidence of a continuum associated with the extreme red system.

Vibrational Analysis

In Table I the frequencies of band heads in the main system are arranged in a v', v'' matrix showing G' and G'' differences. These are frequencies of the $Br^{79}Br^{81}$ molecule which is twice as abundant as either of the symmetrical

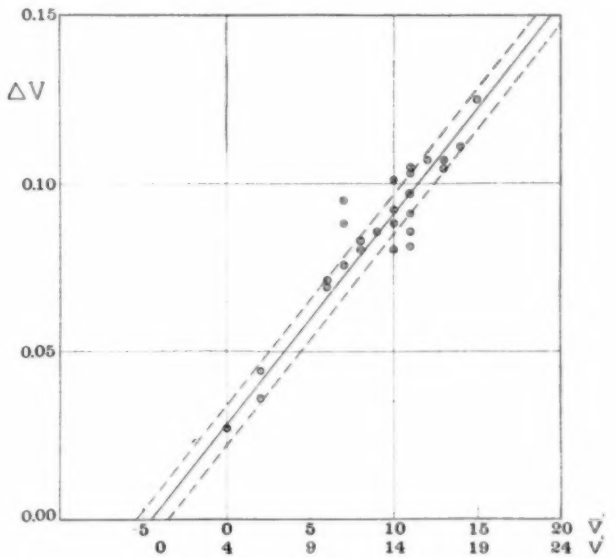

Fig. 1.

molecules, Br_2^{79}, and Br_2^{81}. The $\bar{v}'$ numbering of column 2 is a provisional numbering adopted prior to the deduction of the v' numbering (column 1) from the isotope effect. This provisional numbering is identical with Kuhn's[1] v' numbering from 0 to 11 but differs by 5 units for higher states. There is no change in the v'' numbering.

For the purpose of deriving the quantum numbering of the upper state use has been made of the following equations:[5]

$$\delta\nu = \delta G_v' - \delta G_v'' \tag{1}$$

$$\delta G_v'/\omega_v = \Delta v = (\rho - 1)(v' + \tfrac{1}{2}) \tag{2}$$

The correctness of the v'' numbering is assumed, so that for each observed

[5] G. E. Gibson, Zeits. f. Physik **50,** 692 (1928); J. Patkowski and W. E. Curtis, Trans. Faraday Society **25,** 725 (1929); R. T. Birge, Vibrational Isotope Effect, unpublished. Birge here suggests the use of δ to express an isotope displacement.

shift, $\delta\nu$, the value of $\delta G_v'$ may be found from equation (1), and the corresponding value of Δv from Eq. (2). These values of Δv, when plotted against an arbitrary numbering, $\bar{v}'$, should lie on a straight line of slope $(\rho-1)$ and having an intercept on the $\bar{v}'$ axis equal to $\bar{v}'-(v'+\frac{1}{2})$.

TABLE II. *Observed isotope shifts and related quantities.*

v', v''	$\delta\nu$	$\delta G''$	$\delta G'$	w_v	Δv	$\bar{v}'$
5,4	4.8	8.82	4.0	147	0.027	1
6,4	3.7	8.82	5.1	144	0.036	2
6,4	2.5	8.82	6.3	144	0.044	2
6,5	4.4	10.70	6.3	144	0.044	2
11,3	4.2	6.90	11.1	126	0.088	7
11,3	5.0	6.90	11.9	126	0.095	7
10,2	4.2	4.97	9.2	129	0.071	6
10,2	3.9	4.97	8.9	129	0.069	6
11,2	4.2	4.97	9.2	126	0.073	7
14,3	3.5	6.90	10.4	113	0.080	10
14,3	3.0	6.90	9.9	113	0.088	10
12,2	3.4	4.97	8.4	123	0.069	8
12,2	4.9	4.97	9.9	123	0.080	8
14,2	4.1	4.97	9.1	113	0.080	10
15,2	4.4	4.97	9.4	110	0.086	11
13,1	7.2	3.00	10.2	119	0.086	9
14,1	8.4	3.00	11.4	113	0.101	10
18,2	5.9	4.97	10.9	98	0.111	14
15,1	7.1	3.00	10.1	110	0.092	11
15,1	8.6	3.00	11.6	110	0.105	11
19,2	6.8	4.97	11.8	95	0.125	15
16,1	8.4	3.00	11.4	106	0.107	12
17,1	7.9	3.00	10.9	102	0.107	13
17,1	8.6	3.00	11.6	102	0.104	13
15,0	10.3	1.01	11.3	110	0.103	11
15,0	7.9	1.01	8.9	110	0.081	11

TABLE III. *Frequencies of band heads in the extreme red system, in cm^{-1}.*

v' \ v''	1	2	3	4	5	$\Delta G'_{v+\frac{1}{2}}$
0			13773.0	13457.2	13145.3	112.5
1			13885.3	13572.1	13257.9	103.5
2		14307.2	13989.3	13674.5	13361.0	95.4
3			14084.0	13769.9	13457.2	89.9
4		14490.6	14173.8	13859.7	13547.4	80.5
5		14570.3	14255.2	13940.4	13627.6	75.0
6		14647.3	14330.5	14013.9	13701.9	68.1
7		14714.3	14398.0	14084.0	13769.9	59.5
8		14775.5	14455.9	14143.1	13829.8	54.5
9		14828.5	14511.8	14197.7		50.0
10	15197.5	14877.5	14562.6	14247.9		44.1
11	15241.8	14922.4	14604.8			38.2
12	15280.9	14960.1	14643.7			35.4
13	15316.5	14996.2	14678.1			31.3
14	15347.1	15028.2				29.5
15	15376.6	15057.6				27.3
16	15403.4	15085.4				24.2
17	15427.6	15109.6				22.0
18	15450.0	15131.1				19.6
19	15470.0	15150.3				18.9
20		15169.2				16.3
21	15503.0	15185.5				
$\Delta G''_{v+\frac{1}{2}}$	319.2	316.5	314.5	312.6		

In this work the isotope shifts with respect to the $Br^{79}Br^{81}$ heads are considered. The two values of $(\rho-1)$, though opposite in sign, are practically equal in magnitude: 0.00625. In Table II a few of the most reliable isotope shifts are given, together with the corresponding values of $\delta G_v'$, $\delta G_v''$, and Δv. The latter are plotted, as described above, in Fig. 1. The dotted lines cor-

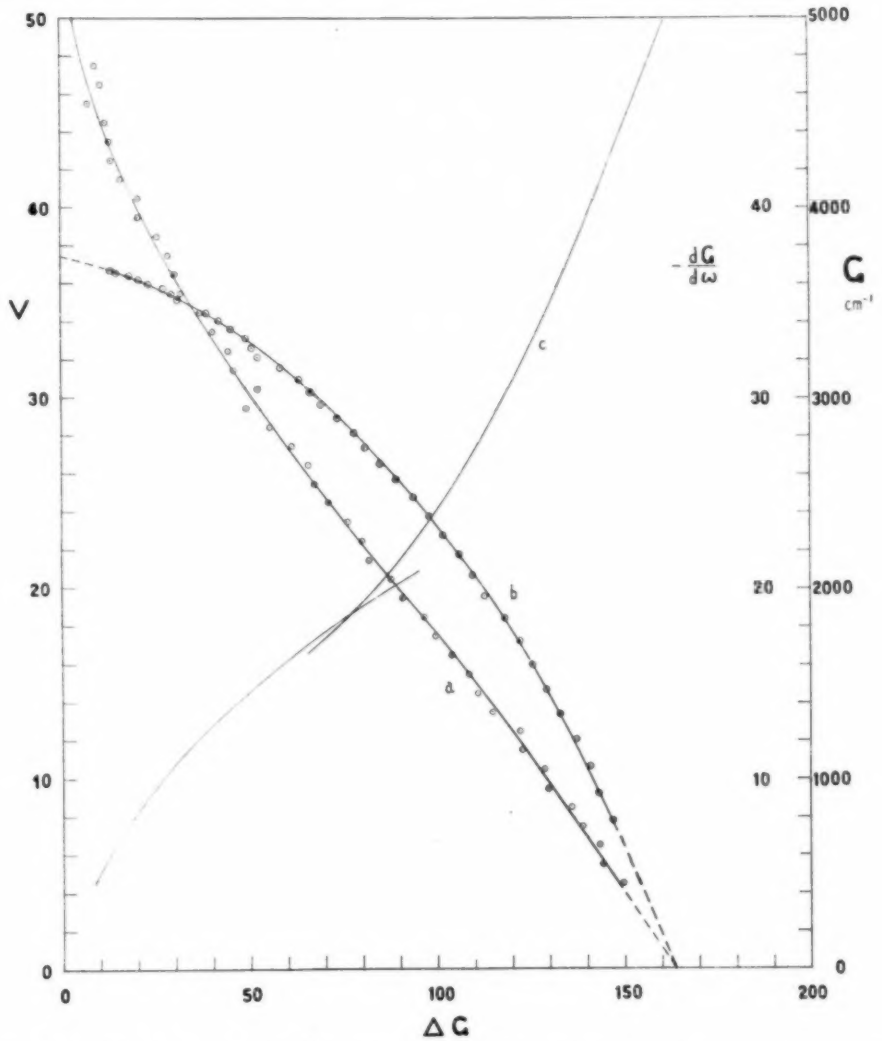

Fig. 2. (a) $\omega:v$, (b) $G:\omega$, (c) $dG/d\omega:\omega$ curves for the upper level of the main system of bromine.

respond to $v'-\bar{v}'=3$ and 5, while the v' numbering adopted differs from the arbitrary numbering by 4 units.

The upper level of this system shows the features which Birge[6] has found to be typical of the halogens. Thus the $\omega:v$ curve (curve *a* of Fig. 2) exhibits a point of inflection at $v=21\pm2$, while the vibrational energy, G, as a func-

[6] R. T. Birge, Trans. Faraday Society **25**, 707 (1929).

tion of ω is roughly parabolic. The derivative, $dG/d\omega$, plotted against ω as curve c, was calculated from least squares solutions over two separate portions of the data. The errors are such that it is difficult to decide whether this curve should be made up of two linear portions, but at any rate the curvature toward the origin at small values of ω is analogous to the behaviour of iodine[7] and is to be expected. For values of v' less than 21 the band heads may be represented by the formula:

$$\nu = 15,831.2 + (163.81v' - 1.59v'^2 - 0.0087v'^3) - (322.71v'' - 1.15v''^2)$$

The vibrational analysis of the extreme red system is given in Table III. The v'' numbering is based on the G'' differences, which agree well with those for the main system (cf. Table I), and on the heat of dissociation. No bands of the $v''=0$ progression could be detected. The intensities are distributed on a rather wide Condon parabola and the maximum intensity in this progression is to be expected at or near the convergence. This region of the spectrum is obscured by strong bands of the main system and by continuous absorption from higher progressions of the extreme red system.

No satisfactory measurement of the isotope effect in this system have been obtained and the v' numbering is, therefore, arbitrary. Evidence of qualitative nature indicates that this numbering should be increased by 4 ± 2 units. This evidence consists of observations of the point of sharpest band heads in each v' progression from which, by Eqs. (1) and (2), the true numbering can be obtained assuming that these are the points where the isotope effect changes sign. In the case of the main system preliminary observations of this kind gave a result in error by only one unit. The isotope effect changes much less rapidly in the extreme red system and such points do not appear well defined. In the higher progressions, $v''=5$, 4, and possibly 3, the relations between $\delta G'$ and $\delta G''$ are such that points of zero isotope shift are not to be expected but instead only a minimum.

The data for the upper levels are not capable of representation by a simple polynomial. From $v'=0$ to $v'=11$ the ω:v curve is approximately linear, or has slight positive curvature. In this interval the observed band heads may be expressed approximately by

$$\nu = 14734 + (112.8v' - 3.4v'^2) - (322.7v'' - 1.15v''^2).$$

Above $v'=11$ a pronounced positive curvature sets in but the curve later flattens out somewhat and a smooth extrapolation from the levels $v'=13$ to $v'=21$ results in the value 1.963 volts for the heat of dissociation. This is in excellent agreement with the value 1.961 volts calculated from the convergence of the main system. In this calculation the value, 3685 cm^{-1},[8] was used for the separation of the ^2P states of the bromine atom. This agreement, it need hardly be pointed out, affords satisfactory proof that the upper level of the extreme red system dissociates into two normal atoms. The probable error of the mean of these values for the heat of dissociation, 1.962 volts is

[7] W. G. Brown, Phys. Rev. **38**, 709 (1931).
[8] L. A. Turner, Phys. Rev. **27**, 397 (1926).

believed to be considerably less than the error given by Sponer,[9] whose value, 1.961 ± 0.008 volts, is derived from the measurements of Kuhn.[1]

No analysis of the fine structure of the bromine bands has been published. It may be worthwhile, therefore, to state here the result of a calculation of the moment of inertia from chemical data, namely the measurements by Bodenstein[10] of the dissociation of bromine at high temperatures. Using the equation of Gibson and Heitler,[11] modified slightly to take into account a small fraction of atoms in the $^2P_{1/2}$ state at the temperatures employed in the experiments, a value of I'' was calculated for each of eleven observations above 1400°K. These gave a mean value of 445×10^{-40} g·cm² and a probable

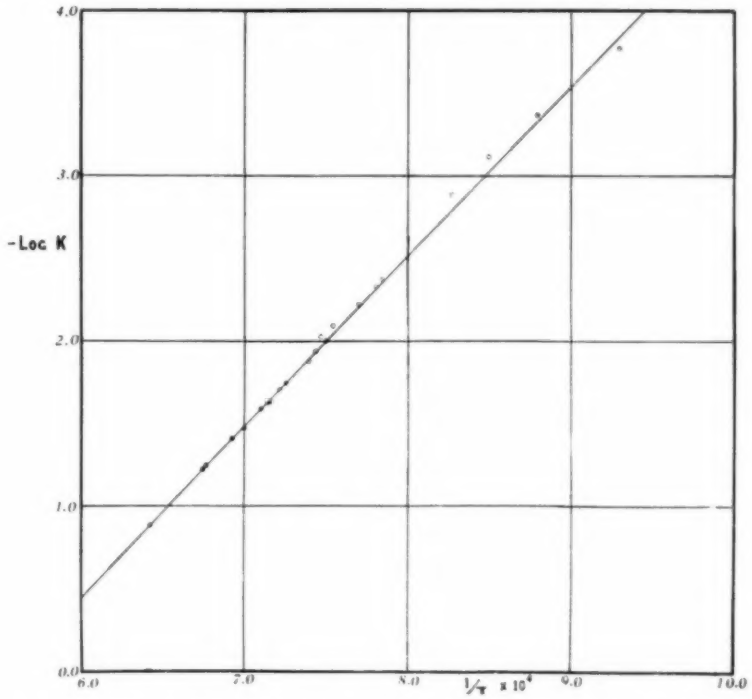

Fig. 3. Logarithm of the equilibrium constant for the dissociation of bromine plotted against the reciprocal of the absolute temperature. The curve was drawn with the aid of the Gibson and Heitler equation but is based on the experimental values at high temperatures.

error, based on internal consistency alone, of ± 3 g·cm². The corresponding nuclear separation is 2.54A. Wierl[12] obtained 2.28A by the method of electron diffraction. In Fig. 3 the experimental values of log K for the reaction $Br_2 = 2$ Br are plotted against the reciprocal of the absolute temperature. The curve was drawn with the aid of the Gibson-Heitler equation using the value of I'' given above.

[9] H. Sponer, Landolt-Bornstein Tabellen, Ergänzungsband. Values quoted by J. Franck, Naturwiss. **10**, 217 (1931).

[10] M. Bodenstein, Zeits. f. Elektrochemie **22**, 327 (1916).

[11] G. E. Gibson and W. Heitler, Zeits. f. Physik **49**, 465 (1928).

[12] R. Wierl, Ann. d. Physik **8**, 521 (1931).

In conclusion it might be pointed out that the existence of a separate band system in the red portion of the bromine absorption spectrum has been commented on by a number of investigators although no analysis has been given. Thus Nakamura[13] states that a second band system appears at high temperatures but the measurements given by him appear to be entirely measurements of higher progressions of the main system. Only a few correspond to the measurements of the extreme red system contained herein.

The writer is deeply indebted to Professor G. E. Gibson for his interest and advice, and to Professor R. T. Birge for the privilege of examining the manuscript of a paper to be published by him on the isotope effect.

[13] G. Nakamura, Footnote 4, References to earlier observations are given.

AN INFRARED ABSORPTION BAND SYSTEM OF IODINE

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(Received August 7, 1931)

Abstract

A vibrational analysis is given for a group of weak bands observed between 8300A and 9300A in the absorption spectrum of saturated iodine vapor at temperatures between 80° and 150°C. The system is analogous to the extreme red system of bromine, being due to transitions from the normal state to an electronic state of small D value ($\sim$0.08 volts) dissociating into normal atoms. A region of continuous absorption, presumably associated with the band system, and having a maximum at 7320 ± 50A has been observed.

IN A preliminary account[1] of the results contained in the previous paper reference was made to a group of bands in the infrared absorption spectrum of iodine similar to those observed in the extreme red spectrum of bromine. At that time the bands had been photographed with the 10 ft. grating of the Chemical Laboratory, University of California but the number of bands appearing on these plates was insufficient for a vibrational analysis. The experiments have been repeated at this laboratory using a 5 ft. grating (Rowland mounting) which gave a dispersion, in the first order, of 16.9A/mm. While the smaller dispersion of this instrument was more suitable for the observation of band heads the accuracy of measurements is somewhat less on this account, and is further limited by the fact that the band heads in general are not well defined. They do not compare in sharpness, for example, with the visible iodine bands.

A Pyrex absorption tube, 150 cm in length, contained excess solid iodine and was equipped for electrical heating. The two ends of the tube were maintained at temperatures slightly higher than the centre portion in order to prevent condensation on the windows, so that the actual temperatures of the vapor cannot be stated with accuracy. At relatively low temperatures, about 50°C, a weak continuum having a maximum at 7320 ± 50A was observed. Bands of the visible system extended nearly up to this point but could not be observed beyond. At higher temperatures (and pressures) the region of continuous absorption broadens and becomes more intense. The infrared bands begin to appear at about 80° and show with good intensity at 150°.

The photographic emulsions were sensitized to the infrared by the method used by Kiess and deBruin[2] in their work on the arc spectrum of chlorine. This procedure, in the opinion of the writer, is more satisfactory than the use of neocyanine alone even though subsequently hypersensitized in ammonia. With a 500 watt tungsten lamp as a source, exposures of 15 minutes gave good blackening to 8800A, while with a six hour exposure, bands could be measured to 9300A. Of course the principal advantages of the mixed dyes are the extension of sensitivity toward shorter wave-lengths, and the greater uniformity.

* National Research Fellow.

[1] W. G. Brown, Phys. Rev. **37**, 1007 (L) (1931).

[2] Kiess and DeBruin, U.S. Bur. Standards J. Res. **2**, 1117 (1929).

Table I, giving the vibrational analysis in the form of a v', v'' matrix diagram, does not include about twenty measurements which can be assigned, somewhat arbitrarily, in the analysis but which appear to be false heads formed by the partially resolved fine structure. The G'' differences agree satis-

TABLE I. *Frequencies, in cm^{-1}, of band heads in the infrared system of iodine.*

v' \ v''	2	3	4	5	$\Delta G'_{v+\frac{1}{2}}$
0		11170	10957	10751	42
1		11212	11004	10790	40
2		11249	11040	10831	38
3			11078	10870	36
4	11535	11325	11115	10905	34
5	11569	11359	11149	10942	32
6		11391	11181	10973	31
7	11635	11423	11212	11004	29
8	11663		11242	11032	26
9	11693	11480	11268		25
10	11715	11505	11295		24
11		11528	11319		26
12	11764	11554	11345		21
13	11786	11575	11365		22
14	11807	11596	11388		21
15	11827	11618	11408		19
16	11847	11635			16
17	11861	11652			17
18	11879	11669			16
19	11896	11685			15
20	11910	11700			14
21	11924	11715			12
22	11936				
$\Delta G''_{v+\frac{1}{2}}$	211	210	209		

factorily with those of the visible system but are not sufficiently accurate to determine the correct v'' numbering. However this can be determined unambiguously from the heat of dissociation[3] since the extrapolation from the observed levels to the point of convergence is small. The v' numbering is arbitrary and must remain so since there are no isotopes of iodine. Like the upper level of the extreme red system of bromine the ω:v curve exhibits positive curvature throughout. The following formula represents the band heads approximately and gives the correct heat of dissociation.

$$\nu = 11{,}803 + (43.0v' - 1.0v'^2 + 0.008v'^3) - (214v'' - 0.6v''^2)$$

The corresponding value of D', 0.08 volts, represents a lower limit, because of the uncertainty in the v' numbering, but is probably correct in order of magnitude. In constructing the potential energy curves of Fig. 1 it is assumed that the continuous absorption at 7320A corresponds to the most probable transition, as shown by the arrow, thus fixing one point on the curve for the upper level of the infrared system. The value of r_e found in this way is 3.2A. For the normal level and for the upper level of the visible bands the more accurate data given by Birge[4] are used.

[3] W. G. Brown, Phys. Rev. **38**, 709 (1931).
[4] R. T. Birge, I.C.T. **V**, 411 (1929).

Mulliken,[5] in his theoretical interpretation of the visible halogen bands, predicted the existence of certain molecular states having small D values and dissociating into normal atoms. These are the 0_u^-, 1_u, and 2_u components of a $^3\Pi$ multiplet. The new levels of bromine and iodine may thus be one of these but it is difficult to understand, if this is so, why these transitions are weak. The form of the potential energy curves explains, partially at least, the low intensity of the band systems, but not the fact that in iodine the continuum presumably associated with the band system is also weak. The transition, $0_u^- \leftarrow {}^1\Sigma_g^+$, not permitted with case c coupling, would be weak if the true state of affairs were intermediate between case a and case c, but in this case the stronger transition, $1_u \leftarrow {}^1\Sigma_g^+$, should also be observed. There are, however, other states derivable from two normal halogen atoms which may come into consideration.

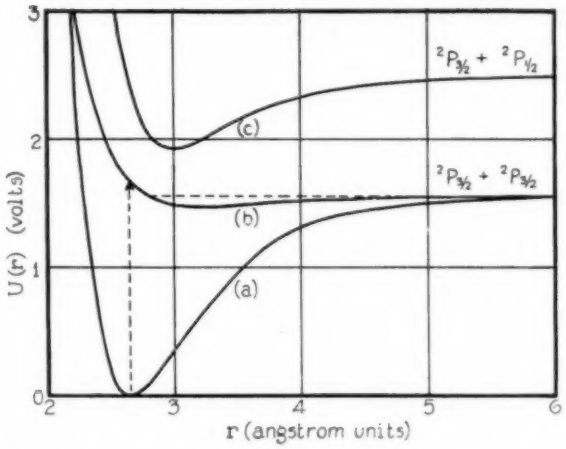

Fig. 1. Potential energy curves for (a) the normal state, (b) the upper level of the infrared system, and (c) the upper level of the visible system of iodine, drawn with the aid of the Morse function.

Pringsheim and Rosen,[6] investigating the infrared absorption spectrum of iodine, apparently failed to observe the system described above. Of the series from 13217 cm^{-1} to 11737 cm^{-1} observed by them, and ascribed to a new band system, only two members fall in the region covered by the present measurements. These authors, assuming that the final states of the high and low temperature ultraviolet absorption bands were identical, deduced the existence of a level lying 7000 cm^{-1} above the normal level. This state must have the same symmetry as the normal state and therefore cannot be the upper level of the infrared system. However, the correctness of their analysis has been questioned by Sponer and Watson[7] who present an alternate assignment of the high temperature ultraviolet bands. Nakamura's[8] measurements of the iodine absorption spectrum do not extend beyond 8000A.

[5] R. S. Mulliken, Phys. Rev. **36,** 669, 1440 (1930).
[6] P. Pringsheim and B. Rosen, Zeits. f. Physik **50,** 1 (1928).
[7] H. Sponer and W. W. Watson, Zeits. f. Physik **56,** 184 (1929).
[8] G. Nakamura, Mem. Coll. Sci., Kyoto Imp. Univ. **A9,** 315 (1926).

ULTRAVIOLET BANDS OF CO IN THE ELECTRODELESS RING DISCHARGE

By H. P. Knauss and J. C. Cotton
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(Received July 11, 1931)

Abstract

The relative intensities of the band systems of CO in the region 2900 to 2150A obtained in an electrodeless ring discharge at various pressures were observed, and compared with Geissler tube spectra. A continuous wave oscillator using 100 watts at 6400 kilocycles was used to produce the ring discharge.

Cameron bands. This system was well developed in the ring at low pressures, in contrast with results obtained by Herzberg who failed to obtain it in the ring excited by damped oscillations. The 0–1 band at 2157A was observed in addition to previously known members of the system.

Bands of the CO^+ ion. In the ring at all pressures, the first negative bands (CO^+) were strong, indicating the presence of ions in the ring. The comet-tail bands, due to the same ion, appeared only at low pressures.

Fourth positive bands. This system is very strong in the Geissler tube, and in the ring at high pressures. At low pressures it is very weak in comparison with the Cameron bands.

The observations show that the electrodeless ring discharge affords a means of selective excitation of certain band systems, and should prove of value in the study of overlapping systems.

Introduction

THE investigation of which this work is a part, has for its purpose a study of the effectiveness of the electrodeless ring discharge maintained by a continuous wave oscillator as a source of band spectra, in which various band systems may be emphasized or suppressed by controlling the conditions of the discharge.

Factors under control in this form of discharge include the frequency and power input of the oscillator, and the pressure of the gas. The results here presented were obtained by varying only the pressure of the gas, keeping the frequency and the power input fixed. Comparison is made with spectra obtained in the conventional π-shaped Geissler tube.

Carbon monoxide was used in this work because of the large number of known bands in accessible portions of the spectrum. The bands here considered in detail lie in the region 2150 to 2900A.

An exhaustive study of CO bands was made by Herzberg[1] in 1928; however he used the electrodeless ring discharge maintained by damped oscillations of a condenser discharging through a spark gap, and apparently obtained a less energetic discharge than that produced by our tube-driven oscillator.

[1] G. Herzberg, Zeits. f. Physik **52**, 815 (1928).

Description of Apparatus

Oscillator. A wiring diagram of the oscillator is given in Fig. 1. The tube was a UX-852 with a maximum safe plate dissipation of 100 watts. The plate supply was obtained by full wave rectification of the high tension output of two transformers connected in series, using a pair of kenotrons. The plate voltage was controlled by inserting resistance in series with the primaries of the transformers. The maximum plate potential which could be used was about 1250 volts; higher voltages caused sparking across the variable air condenser *C*. The plate current was about 80 milliamperes, and the oscillating current about 1 ampere.

The inductance of the oscillating circuit was a $5\frac{1}{2}$ turn helix 35 cm in diameter of 1 cm copper tubing, surrounding the sphere in which the discharge occurred. The capacity, as shown in the diagram, was the plate to grid capacity of the tube. The variable air condenser *C* acted as a blocking con-

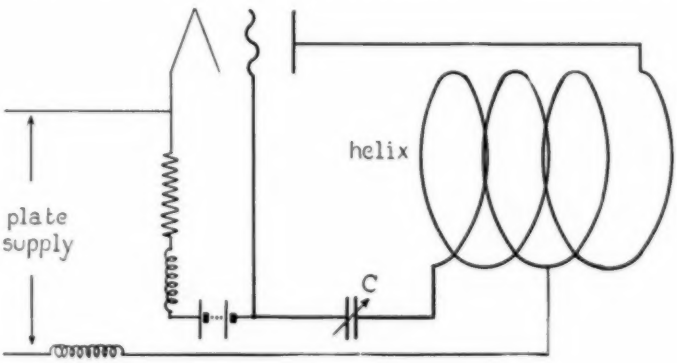

Fig. 1. Wiring diagram of 32 meter oscillator.

denser, and had only a small effect on the frequency, amounting to a 7 percent change in frequency for extreme settings of the condenser. The wavelength was 32 meters, corresponding to a frequency of 9400 kilocycles.

Discharge bulb. The electrodeless discharge was obtained in a 12 liter Pyrex flask with a diameter of 29 cm, provided with a tangential neck with a quartz window sealed on by means of a quartz to pyrex graded seal. The position of the helix surrounding the sphere could be adjusted so as to have the window well illuminated by the discharge.

Gas generator. The carbon monoxide was obtained by dropping formic acid into warm concentrated sulfuric acid. It was purified over KOH, dried over P_2O_5, and admitted into the discharge bulb through stop cocks. From the discharge bulb extended connections to a liquid air trap, a McLeod gauge, a mercury cut-off, a mercury diffusion pump, and a backing pump. For comparison purposes, a H-shaped Geissler tube with a quartz window was attached to the system. It was excited by 60 cycle A. C. at 1100 volts through a 5000 ohm resistor.

Spectrograph. The spectrograph was a Féry prism type, giving a spectrum 11 cm long for the range 2150–2900A. In the absence of means for im-

pressing a wave length scale or a comparison spectrum on the film, a wave-length scale was made to fit microphotometer records of an iron arc spectrum. With the aid of mercury lines and known bands, the scale could be fitted to microphotometer curves and to enlargements of the spectra studied. This method permitted errors of a few Angstrom units, but was considered sufficiently reliable for purposes of identification. Greater accuracy in wave-length measurements will require the construction of a source to be used with the grating spectrographs of the laboratory.

Experimental Procedure

As a result of a number of experiments in which discharge conditions were varied somewhat at random, it was found that the most interesting bands in the region studied were obtained at high energy input[2] at various pressures of the gas. Accordingly the series of exposures reproduced in Fig. 2 was made.

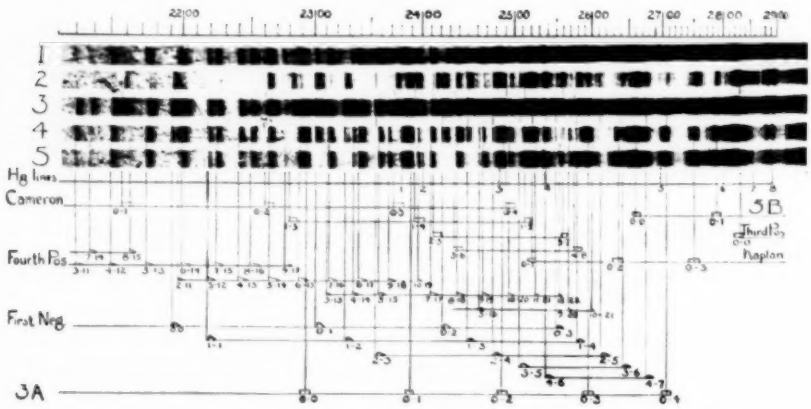

Fig. 2. Spectra of CO in the Geissler tube and the ring discharge.

Exposure No.	Source	Pressure (mm)	Time
1	Geissler tube discharge	0.15	6 min.
2	Electrodeless ring discharge	0.0002 to 0.0013	4.5 hr.
3	Electrodeless ring discharge	0.012 to 0.14	2.0 hr.
4	Electrodeless ring discharge	0.6 or more	0.5 hr.
5	Geissler tube discharge	0.42	8 min.

Marked lines due to mercury, wave-lengths from International Critical Tables Vol. 5.

1	2378.3	3	2482.7	5	2698.9	7	2847.7
2	2399.4	4	2536.	6	2803.6	8	2893.6

Exposures 1 and 5 were made with the Geissler tube for comparison; the pressure for exposure 1 (0.15 mm) being that for maximum brilliancy of the discharge with the voltage applied to the tube. The range through which the tube operated on 1100 volts was between about 0.06 and 0.42 mm pressure.

The electrodeless discharge, on the other hand, could be maintained at pressures as low as 0.0002 mm and up to several mm. Exposures 2, 3, and 4

[2] H. P. Knauss and J. C. Cotton, Phys. Rev. **36,** 1099 (1930).

are typical of low, intermediate, and high pressure discharges respectively. A scale of wave lengths and identifications of bands are included in Fig. 2. Exposure times have been selected to compensate somewhat for differences in the brightness of the sources.

Results and Discussion

Bands emphasized by ring discharge. The first negative group of carbon[3] appears strongly in the ring discharge at all pressures. This system is emitted by the CO^+ ion, and thus indicates the presence of these ions in the ring discharge. In the Geissler tube, on the contrary, the ions apparently are pulled into the electrodes by the electric field, and are present in smaller numbers. These bands were observed by Herzberg[1] in the electrodeless discharge maintained by damped oscillations.

Bands emphasized by low pressures. Attention has already been called[2] to the occurrence of the Cameron bands[4] in the ring discharge at low pressures. Herzberg[1] failed to obtain these in spite of long exposures at low pressures. It is probable that the excitation was not intense enough in his case to produce the Cameron bands, since exposures made with less power in our oscillator also failed to bring out these bands. This system was discovered[4] in neon with CO present in small quantities. Hopfield and Birge[5] obtained Cameron bands in absorption in pure CO. (They did not obtain them in emission, our statement[2] to the contrary being a misreading of the abstract[5] of their preliminary report.)Duffendack and Fox[6] tried unsuccessfully to obtain the Cameron bands in the low voltage arc.

Of the bands labelled in Fig. 2, all had previously been identified, with the exception of the $0-1$ Cameron band. This band is clearly present in exposures 2 and 3 (low and intermediate pressures, respectively) but absent in exposure 4 (high pressure) and in the Geissler spectra, exposures 1 and 5. The other bands of the system show a similar behavior in the original spectrum photograph, although this may not be obvious in the reproduction. The disappearance of these bands at high pressures indicates that the molecule leaves the initial state more readily by impact than by radiation, when the impacts are frequent.

The comet-tail system of CO (in the visible region, not included in Fig. 2) is strongly developed in the ring discharge at low pressures. This system was obtained also by Herzberg.[1]

The fourth positive bands are strong in the Geissler discharge and in exposure 4 (high pressure), but almost entirely absent in exposure 2 (low pressure). This illustrates again the dependence of relative intensities of bands on excitation conditions, so that disagreements of intensity estimates recorded[7,8] by various workers are not surprising.

[3] C. M. Blackburn, Proc. Natl. Acad. Sci. **11**, 28 (1927).
[4] H. B. Cameron, Phil. Mag. **1**, 405 (1926).
[5] J. J. Hopfield and R. T. Birge, Phys. Rev. **29**, 922 (1927).
[6] O. S. Duffendack and G. W. Fox, Astrophys. J. **65**, 214 (1927).
[7] R. T. Birge, Phys. Rev. **28**, 1157 (1926).
[8] R. S. Estey, Phys. Rev. **35**, 309 (1930).

The bands discovered by Kaplan[9] were originally observed in a Geissler tube containing hydrogen with a trace of CO. In our photographs they appear in both the ring and the Geissler discharges in pure CO. We also obtained them in the ring discharge in hydrogen at low pressure with a trace of CO. It is of interest to note that the Cameron bands also appeared under the latter conditions, although they were not present in the Geissler discharge observed by Kaplan.

The 3A bands, like the fourth positive system, are very much weakened at lower pressures. The 5B system is affected in the same way, but not nearly as much.

Conclusions

Two principal conclusions about the electrodeless ring discharge as a source of bands may be pointed out. The first, which was established by earlier work, with damped oscillations causing the ring, is that spectra of molecular *ions* are enhanced in this source. The second, which was suspected before, but not fully realized experimentally, is that "low pressure bands" or bands which involve transitions with small probabilities can be brought out in the ring at low pressures, since this source permits reasonable intensities of discharge at pressures considerably lower than those at which Geissler tubes operate. The power available for excitation in the earlier work apparently was insufficient, a limitation which is readily overcome by means of the vacuum tube.

The writers are pleased to have had an opportunity to discuss their results with Professor R. T. Birge during his stay here.

[9] J. Kaplan, Phys. Rev. **35,** 1298 (1930).

INTENSITIES OF BALMER EMISSION LINES IN STELLAR SPECTRA

By Otto Struve and Harold F. Schwede
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(Received August 3, 1931)

Abstract

Contours of the Balmer emission lines in the spectra of fourteen stars of spectral class *Be* have been measured on twenty-seven spectrograms. In many stars the lines are broad and flat-topped, with steep outer edges, while in others they are double. The contours are explained by Doppler effect caused by the rotation of a nebula surrounding the star. The mean relative total intensities are: $\beta:\gamma:\delta:\epsilon = 10:6.2:5.2:(5.4)$. The slow decrement in intensity agrees with the hypothesis that the bright lines are caused mostly by recombination. Lines produced in this way must be strongest (other things being equal) in a medium containing a maximum number of atoms of the next stage of ionization. This agrees with the observed strength of the emission lines of Fe II and of H in the earlier subdivisions of spectral class *B*.

Introduction

APPROXIMATELY one out of every fifteen stars of spectral class *B*0 to *B*5 (effective temperature 23,000°C to 15,000°C absolute) shows, in addition to the usual absorption-line spectrum, a number of emission lines. Bright Balmer lines are observed most frequently, but occasionally emission lines of Fe II, He I and He II, Mg II, etc., are also present. The emission lines of hydrogen are usually superposed over broad and shallow absorption lines similar to those observed in normal stellar spectra.[1]

Until recently little was known concerning the origin of these bright lines. The normal reversing layer of a star's atmosphere produces absorption lines only.[2] In many stars the emission lines are conspicuously broadened. Attempts have been made by various investigators to attribute this peculiar broadening to pressure or Stark effect. But we now know that in the reversing layer the ionic Stark effect is very powerful and that it causes extremely broad absorption lines of hydrogen having wings sometimes one hundred or more angstroms in extent. The contours of the emission lines, on the other hand, are quite different. Thus, in Fig. 1 the star 25 Orionis has a typical broad emission line, with flat top and steep outer gradients. It seems evident that this type of broadening cannot be due to Stark effect.

A much better representation of the contours may be obtained by assuming that the bright lines originate in a gaseous shell outside the reversing layer of the star. This assumption agrees well with the results of theoretical investigations.[2] The broadening of the bright lines may then be explained as a Doppler effect caused by the rotation of the nebulous shell around the star.

[1] For further details see: O. Struve, Astrophys. J. **73**, 94 (1931) and the original papers by P. W. Merrill, R. H. Curtiss and W. J. S. Lockyer.

[2] S. Rosseland, Astrophysik auf atomtheoretischer Grundlage, p. 198, 1931.

This not only accounts for the peculiar flat-topped contours of the emission lines in such stars as 25 Orionis, but it also explains the doubling of the emission lines in ψ Persei, π Aquarii and many other stars.[3] Furthermore, there appears to be a distinct tendency for broad and widely-separated double emission lines to occur in stars having "dish-shaped" absorption lines. On the other hand, narrow emission lines occur predominantly in stars having

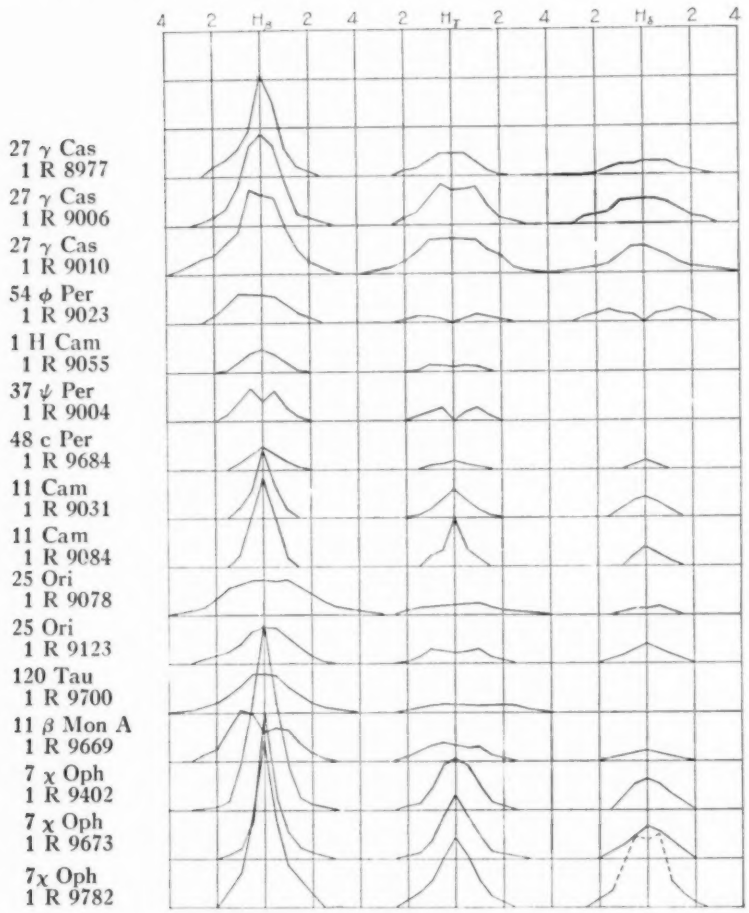

Fig. 1. Contours of hydrogen emission lines in *Be* stars. One division in the abscissa corresponds to two millimeters on the microphotometer tracing. One division in the ordinate corresponds to 0.75 of the intensity of the continuous spectrum adjoining each line. The names of the stars and the numbers of our plates are given at the left.

normal absorption lines of He, Mg II, etc. Since it is believed that dish-shaped absorption lines are produced by rapid axial rotation of the stars, it is impossible to escape from the conclusion that the broadening of the emission lines is also caused by rotation.

Additional evidence in favor of Doppler effect as the primary cause of

[3] O. Struve, Astrophys. J. **73**, 94 (1931).

widening is presented in the work of C. D. Higgs,[4] who found that the contours of the bright Fe II lines in γ Cassiopeiae agree in width with those of the Balmer lines. It would be difficult to explain this similarity in the contours by processes other than Doppler effect.

The rotational hypothesis is sufficiently flexible to account for many of the observed contours of emission lines. Thus, a nebulous ring rotating around a central star would give rise to a double bright line, with steep outer edges.[5] On the other hand, consider a spherical nebula of uniform density, which greatly exceeds the central star in size. Suppose for simplicity that the nebula rotates as a solid. Then, all atoms which lie in a plane that is parallel to the axis of rotation and passes through the line of sight, have the same velocity component in the line of sight:

$$\rho = v \sin i \sin \theta = (x/r)v \sin i$$

where x is the distance of the plane from the central meridian, and r is the radius of the nebula. Since the nebula is transparent to its own light,[6] all atoms lying in the same cross section of the sphere contribute equally to the formation of the line. Consequently, each value of ρ appears in the contour with a weight of

$$(1 - x^2/r^2).$$

If the original contour (not affected by rotation) is very narrow, then the contour of the broadened line is directly given by

$$I = I_0(1 - x^2/r^2). \tag{1}$$

If, however, the original contour is not very narrow, the broadened contour may be evaluated by a process of graphical integration similar to the one used previously for stellar absorption lines.[7] The contour expressed by (1) has a flat top, suggestive of the observed contours of stars like 25 Orionis. In reality, the nebula would not rotate as a solid, since each atom is virtually free to move like a satellite under the attraction of the central force. However, this does not affect our conclusion that flat-topped single lines as well as double bright lines may be explained by the mechanism of rotation.

It should be mentioned that for certain stars the central depression is very narrow and deep. This is probably due to real central absorption in outlying layers of hydrogen (e.g.11β Monocerotis).[8] The doubling caused by rotation is probably responsible for widely-spaced components separated by a diffuse absorption line (e.g.31o Aquarii).

If our conclusion that the bright lines originate in a nebula around the star is correct, it becomes of interest to investigate the mechanism by which

[4] C. D. Higgs, Astrophys. J. **70,** 251 (1929).

[5] O. Struve, Astrophys. J. **73,** 101 (1931).

[6] A. S. Eddington: The Internal Constitution of the Stars, p. 388, 1926.

[7] O. Struve, Astrophys. J. **72,** 13 (1930).

[8] It is, however, difficult to reconcile this view with Eddington's statement that nebulae are transparent to the light of the Balmer lines. For the same reason it would be difficult to attribute the sharp central depressions to absorption in interstellar space.

the lines are excited to emission. It is generally believed that the hydrogen lines emitted by gaseous nebulae are the result of recombination processes.[9] The discovery of W. H. Wright[10] that certain planetary nebulae show a continuous emission spectrum beyond the limit of the Balmer series lends considerable weight to this belief. A similar continuous emission spectrum was found by Ch'ing-Sung Yü[11] in several stars having bright Balmer lines (γ Cassiopeiae, ϕ Persei, χ Ophiuchi, etc.); it is therefore probable that the emission lines in such stars are also caused by recombination.

The observational results of the following section have been derived to provide material for a comparison of the relative Balmer-line intensities in *Be* stars and in gaseous nebulae. For the latter we use the determinations of H. H. Plaskett;[9] the former have not, to our knowledge, been previously determined.

Observational Results

For this investigation we have selected twenty-seven plates of fourteen stars showing fairly strong bright lines. Stars having widely-separated double bright lines were not included, but there are several in which the separation is small or moderate. The quantities to be derived are the relative total energies emitted in the Balmer lines. The spectrograms, calibrated in the usual way with a tube sensitometer, were analysed by means of a thermoelectric microphotometer, and the galvanometer deflections on the tracings were transformed into relative intensities with the use of the calibration marks. An ordinary electric lamp served as a light-source in the sensitometer, and no attempt was made to use separate calibrations for each wave-length. However, from the work of G. R. Harrison[12] and from unpublished tests made at the Yerkes Observatory, it appears that for the particular photographic emulsion (Eastman 40) used by us the characteristic curve does not vary much with wave-length, within the limits here considered.

The intensity measured at any point of the emission line consists of the intensity of the emission line proper plus the residual intensity of the absorption line forming the background on the plate. To allow for this background intensity we have extrapolated the observed wings of the absorption lines towards the center, on the original tracings, and have in each case taken

$$I(\text{emission}) = I(\text{observed}) - I(\text{absorption})$$

There is some uncertainty in the graphic extrapolation of the absorption lines. We have attempted to make them similar to the lines observed in normal *B* stars.[13] Any errors which may have come in would be greatest in the case of comparatively faint emission lines. Stars with strong lines probably

[9] H. Zanstra, Astrophys. J. **65**, 50 (1927); H Zanstra, Zeits. f. Astrophysik **2**, 1 (1931). H. H. Plaskett, Harvard College Observatory, Circular No. 335, J. A. Carroll, Monthly Notices of the Royal Astronomical Society **90**, 588 (1930). A. S. Eddington; The Internal Constitution of the Stars, p. 388, 1926.

[10] W. H. Wright, Nature **109**, 810 (1922).

[11] Ch'ing-Sung Yü, Publications of the Astronomical Society of the Pacific **39**, 112 (1927)

[12] G. R. Harrison, J.O.S.A. **19**, 267 (1929).

[13] C. T. Elvey, Astrophys. J. **71**, 191 (1930).

give more reliable results. It is surprising that in several stars the central absorption, which is well visible on the original negatives, is nearly lost by allowing for the intensity of the background. In other stars, certain fine details visible on the plates were lost in the unavoidable process of smoothing during the measurements, but since it was our intention to get total energies we did not attempt to preserve these details. Nevertheless the differences in the shapes of the lines are well visible in the contours: some are narrow and

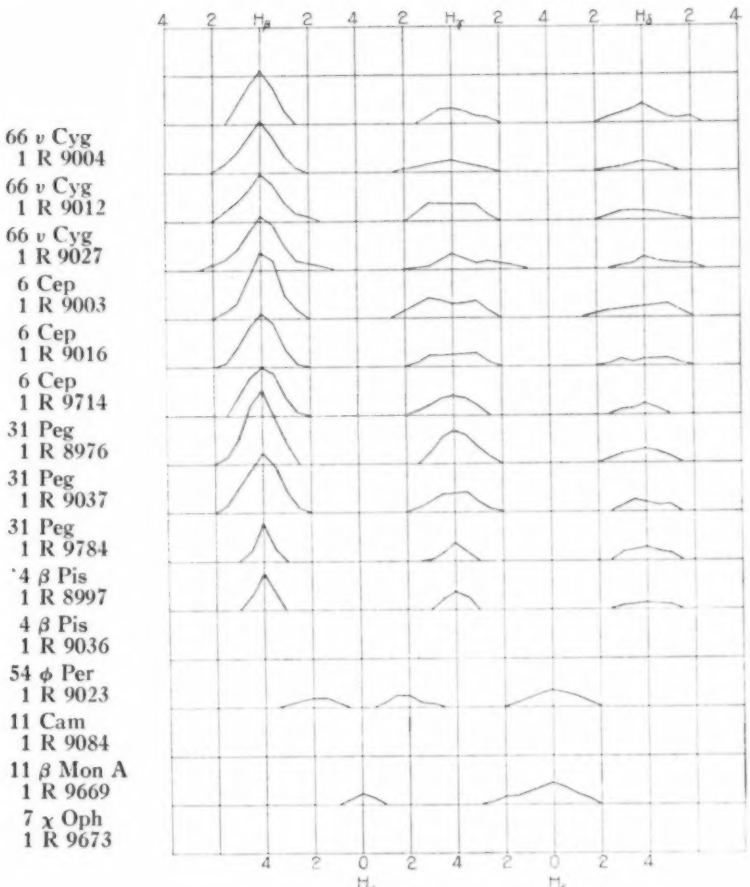

Fig. 2. Continuation of Fig. 1. The four lines at the bottom represent $H\varepsilon$ in four stars.

have peaks in the centers, while others are broadened and flat-topped or even depressed in the centers.

The resulting intensities, as plotted against millimeters on the tracings, are shown in Figs. 1 and 2. One millimeter corresponds to 2.59A at $H\beta$, 1.64A at $H\gamma$, 1.27A at $H\delta$ and 1.09A at $H\epsilon$. For each line the intensity of the adjoining portions of the continuous spectrum is taken as a unit. The transmission factors of the atmosphere and of the optical system are considered the same for the emission line as for the adjoining portions of the continuous spectrum. The true distribution of energy in the continuous spectrum is

known since the stars may be regarded as black-body radiators. Following Russell, Dugan, and Stewart,[14] we have adopted the following temperature scale:

Spectrum:	*B0*	*B1*	*B2*	*B3*	*B5*
Temperature (°K):	23,000	21,000	19,000	17,500	15,000

A small error in the temperature would not appreciably affect our results. Planck's law leads to the following relative intensities in the continuous spectrum:

T(°K)	P_γ/P_β	P_δ/P_β	P_ϵ/P_β
23,000	1.42	1.70	1.87
21,000	1.41	1.68	1.84
19,000	1.40	1.64	1.80
17,500	1.38	1.61	1.76
15,000	1.35	1.55	1.67

Let the observed relative intensities of the continuous spectrum near $H\beta$, $H\gamma$, $H\delta$, $H\epsilon$ be designated by C_β, C_γ, C_δ, C_ϵ, and let the intensities of the emission lines be given by β, γ, δ, ϵ. Then the observed intensities on the plate, referred to the intensity of the continuous spectrum at $H\beta$ as a unit, are:

$$\gamma C_\gamma/C_\beta;\ \delta C_\delta/C_\beta;\ \epsilon C_\epsilon/C_\beta$$

These values multiplied by the transmission factors

$$\frac{P_\gamma C_\beta}{P_\beta C_\gamma};\quad \frac{P_\delta C_\beta}{P_\beta C_\delta};\quad \frac{P_\epsilon C_\beta}{P_\beta C_\epsilon}$$

give the final intensities of the bright lines. The factors C_γ/C_β etc. cancel out.

TABLE I.

Star	Sp	Plate	β	γ	δ	ϵ	$\frac{C\beta}{C\gamma}$	$\frac{C\beta}{C\delta}$	$\frac{C\beta}{C\epsilon}$	$\frac{P\gamma}{P\beta}\gamma$	$\frac{P\delta}{P\beta}\delta$	$\frac{P\delta}{P\beta}\epsilon$
27γ Cas	B0p	IR 8977	10	3.7	2.4	—	0.92	1.52	—	5.25	4.08	—
		9006	10	6.0	4.3	—	0.84	1.30	—	8.52	7.31	—
		9010	10	6.0	3.4	—	0.81	1.32	—	8.52	5.78	—
54ζ Per	B0p	9023	10	2.2	4.8	4.0	1.24	1.39	2.17	3.12	8.16	7.48
1 H Cam	B3p	9055	10	3.9	—	—	1.14	1.59	—	5.38	—	—
37ψ Per	E5p	9044	10	4.4	—	—	1.19	1.82	—	5.94	—	—
48c Per	B3p	9684	10	3.0	2.1	—	0.91	1.02	—	4.14	3.38	—
11 Cam	B3p	9031	10	5.9	4.7	—	1.06	1.19	—	8.14	7.57	—
		9084	10	4.6	2.5	3.6	1.00	1.35	3.33	6.35	4.02	6.34
25 Ori	B3p	9078	10	1.9	0.7	—	0.77	0.95	—	2.62	1.13	—
		9123	10	3.8	3.4	—	0.71	0.96	—	5.24	5.47	—
120 Tau	B3p	9700	10	3.2	—	—	0.82	1.23	—	4.42	—	—
11β MonA	B3p	9669	10	3.6	1.4	0.8	1.01	1.43	3.44	4.97	2.25	1.41
7χ Oph	B3p	9402	10	4.0	2.3	—	1.11	1.75	—	5.52	3.70	—
		9673	10	7.1	4.4	3.5	0.77	1.05	2.44	9.80	7.08	6.16
		9782	10	5.6	6.6	—	1.26	3.12	—	7.73	10.63	—
66ν Cyg	B3p	9004	10	4.0	4.2	—	1.14	1.59	—	5.52	6.76	—
		9012	10	3.4	2.1	—	0.95	1.49	—	4.69	3.38	—
		9027	10	5.7	2.4	—	0.78	1.20	—	7.87	3.86	—
6 Cep	B3p	9003	10	3.2	2.1	—	1.07	1.92	—	4.42	3.38	—
		9016	10	4.7	3.2	—	1.10	2.00	—	6.49	5.15	—
		9714	10	4.0	1.8	—	1.10	1.78	—	5.52	2.90	—
31 Peg	B3p	8976	10	4.5	1.7	—	1.16	1.70	—	6.21	2.74	—
		9037	10	5.2	2.3	—	1.15	1.56	—	7.18	3.70	—
		9784	10	4.3	1.8	—	0.55	1.00	—	5.93	2.90	—
4β Psc	B5p	8997	10	6.3	7.6	—	0.83	1.33	—	8.50	11.78	—
		9036	10	6.4	4.4	—	1.15	1.47	—	8.64	6.82	—
									Mean	6.17	5.16	5.35

[14] Russell, Dugan and Stewart, Astronomy 2, 753 (1927).

The relative intensities of the lines, as they appear on the plate, may be obtained by dividing the values in columns 5, 6, 7 of Table I by the values in columns 8, 9, 10 respectively. The final relative intensities of $H\gamma$, $H\delta$, $H\epsilon$ are shown in columns 11, 12, 13. The intensity of $H\beta$ was taken equal to 10.

An inspection of the contours in Figs. 1 and 2 and of the final intensities in Table I shows that within the rather large accidental errors the relative intensities are about the same in all stars. The similarity is even increased if we consider only stars with strong lines. The mean for all 27 plates is

$$H_\beta : H_\gamma : H_\delta : H_\epsilon = 10 : 6.2 : 5.2 : (5.4).$$

The last value is quite uncertain and has therefore been placed in parenthesis.[15] These relative intensities are probably affected by considerable errors due to the difficulty of separating the emission from the continuous background; but they show that the decrease in intensity towards higher members of the Balmer series is at least as slow as, and perhaps even slower than, that observed in the gaseous nebulae. For the latter, H. H. Plaskett[9] finds, as the mean of eight nebulae:

$$H_\beta : H_\gamma : H_\delta = 10 : 4.25 : 1.83.$$

The comparatively slow decrease in intensity in *Be* stars agrees qualitatively with the result of R. H. Curtiss,[16] who observed the bright lines in 11 Camelopardalis as far as $H\tau$ (the 19th member). In gaseous nebulae, where the observations are easier because of freedom from the continuous spectrum and from broadening, the Balmer series was traced in some cases to $H\xi$ (the 14th member).[17]

Discussion

The relatively slow decrease in the intensities of the Balmer lines in *Be* stars, together with Yü's discovery of continuous emission beyond the series limit, suggests that the Balmer lines are produced by recombination: the hydrogen atoms in the nebulous shell are photoelectrically ionized by absorption of continuous stellar radiation on the high-frequency side of the limit of the Lyman series. The recombination of these free electrons with hydrogen ions causes a number of continuous emissions at the Lyman, Balmer, Paschen, Brackett, etc., limits, and provides each quantum level with a certain population Nn which depends upon the probability of capture into a state with total quantum number n. The excited atoms thus formed lose energy in emitting the various series lines, of which the Balmer lines alone are accessible to observation.

Comparing the *Be* stars with the stimulating stars in gaseous nebulae, we notice that the latter are usually of a spectral class earlier than *B*1 while the former are frequently of class *B*3, *B*5 or even later. The question

[15] The relative intensity of $H\epsilon$ (and to a small extent that of $H\delta$) has been somewhat exaggerated, because in forming the mean we have disregarded all plates on which it could not be measured.

[16] Publications of the Observatory, University of Michigan **3**, 256 (1923).

[17] F. Becker and W. Grotrian: Ergeb. d. exakt. Naturwiss. **7**, 24 (1928).

arises: are these comparatively cool stars sufficiently powerful in their radiation of frequencies greater than $\nu_0 = 32.84 \times 10^{14}$ to stimulate an observable amount of luminosity in the nebulae? The total number of quanta emitted by a star in such frequencies is, according to H. Zanstra:[18]

$$\frac{8\pi^2 R^2 k^3}{c^2 h^3} T^3 \int_{x_0}^{\infty} \frac{x^2}{e^x - 1} dx; \quad x = \frac{h\nu}{kT}$$

Consider two stars: $T_1 = 30{,}000°\text{C}$, and $T_2 = 15{,}000°\text{C}$. The first may be regarded as typical for the gaseous nebulae, the second for the *Be* stars. The ratio of the total energies is

$$\frac{T_1^3}{T_2^3} \frac{\int_{x_0}^{\infty} \frac{x^2}{e^x - 1} dx}{\int_{x_0}^{\infty} \frac{x^2}{e^x - 1} dx} \approx 400.$$

If all radiation beyond ν_0 were absorbed and reemitted in the two nebulae, the gaseous nebula should have a total luminosity 400 times greater than the nebula surrounding the *Be* star. But since in the former the light is spread over a considerable surface, while in the latter it is concentrated in a point-image, it would appear to be possible for a star of class *B*5 to excite a nebula so that it would be perceptible on the spectrogram.

Aside from this difference in total luminosity, there is also a difference in the average kinetic energies of the liberated electrons. According to Eddington[19] the initial electron-temperature is approximately

$$T_0 = (\tfrac{2}{3})T(1 - 1/x_0)$$

where $x_0 = h\nu_0/kT$, and T is the effective temperature of the star. The second term in parenthesis is usually so small that it can be neglected here. The average kinetic energy of the electrons is

$$E = (\tfrac{3}{2})kT_0 \propto T.$$

Consequently in our gaseous nebula the average kinetic energy of the electrons should be twice as great as in the nebula associated with the *Be* star.

It would be tempting to attribute the relatively slower Balmer decrement in *Be* stars, as compared to that of gaseous nebulae, to this difference in electron temperature. But we believe that our observations are not sufficiently accurate to serve as a basis for this deduction. There appears to be no experimental proof of any change in the relative intensities of the lines depending upon electron-velocities. Carl Kenty[20] and Miss Hayner,[21] have found that the line-intensities decrease rapidly with increasing electron-

[18] H. Zanstra, Astrophys. J. **65,** 53 (1927).

[19] A. S. Eddington: The Internal Constitution of the Stars, p. 377, 1926.

[20] Carl Kenty, Phys. Rev. **32,** 624 (1928).

[21] Lucy J. Hayner, Zeits. f. Physik **35,** 365 (1926).

velocity, but their observations do not settle the question whether the relative intensities remain unaltered or not. In the central blue ring of the electrodeless discharge G. Herzberg[22] found the following intensities:

$$\alpha:\beta:\gamma:\delta:\epsilon = 1.00:0.95:0.40:0.14:0.05$$

In the outer red ring he found:

$$\alpha:\beta:\gamma:\delta:\epsilon = 1.00:0.25:0.08:0.020:0\cdot 010.$$

This difference has been interpreted[23] as being due to differences in the relative velocities of the free electrons, but there is no certainty that recombination alone is responsible for the lines throughout the entire cross section of the discharge tube.

A recent theoretical investigation by E. C. G. Stueckelberg and P. M. Morse[24] defines the effective cross-section of recombination

$$q = \sum_{n,l} A(nl)\cdot 10^{-20}\cdot Z^2/V$$

where V is the energy of the electrons. The values of $A(nl)$ were computed by Stueckelberg and Morse, and are practically independent of V. The sums $\Sigma_l A(nl)$ should be proportional to the populations in the various states of total quantum number n:

n	1	2	3	4
$\sum_l A(nl)$:	0.227	0.143	0.104	0.081 .

J. A. Carroll[25] has shown how the expected intensities of the bright lines may be computed by means of the values of $\Sigma_l A(nl)$ and of the transition probabilities computed by Francis G. Slack.[26] Unfortunately the theoretical $\Sigma_l A(nl)$ have been given only for small values of n, and the computation has therefore not been carried out. However, it appears that the expected Balmer decrement for recombination is even slower than that observed for the *Be* stars. This applies of course equally well to the observational data concerning the gaseous nebulae where there can be no reasonable doubt as to the existence of recombination.

It has been pointed out by B. P. Gerasimovič[27] that the bright lines in *Be* stars do not correspond to the state of ionization of the reversing layer. Thus bright Fe II lines are intense in classes *B5e* and *B3e*, while in ordinary absorption spectra ionized iron vanishes near *B8* and reaches maximum near *F0*. A similar situation occurs for the hydrogen absorption lines which have their maxima at *A0*. If the gases responsible for the bright lines were in thermodynamic equilibrium (similar to that believed to hold for the reversing

[22] G. Herzberg, Ann. d. Physik **84,** 565 (1927).
[23] H. H. Plaskett, Harvard College Observatory, Circular No. 335, 14, 1928.
[24] E. C. G. Stueckelberg and Philip M. Morse, Phys. Rev. **36,** 16 (1930).
[25] J. A. Carroll, Monthly Notices of the Royal Astronomical Society **90,** 588 (1930).
[26] Francis G. Slack, Phys. Rev. **31,** 527 (1928).
[27] Private communication.

layer) we should conclude that their state of ionization is lower than that of the reversing layer which is responsible for the absorption lines. Eddington[28] has shown that the state of ionization in a nebula of temperature T and of density ρ will be the same as that of a gas in thermodynamic equilibrium of the same temperature and of density $\rho\delta$, where δ is the "dilution factor." Since, for constant temperature, lower ionization means greater density, we must have

$$\rho\delta > \rho_0$$

where ρ_0 is the density of the reversing layer. Professor Gerasimovič has pointed out to us that the relative rotational velocities from bright and dark lines show that δ should be of the order of 3. Consequently

$$\rho > \rho_0/\delta = \rho_0/3.$$

This is, of course, altogether too large a density for a nebula.

But the difficulty is only an apparent one. The ionization in the nebula is probably not much lower than in the reversing layer. In the case of recombination the maximum intensity of a line of a given stage of ionization n is reached when the medium contains a maximum number of atoms ionized $(n+1)$ times. Thus the emission lines of Fe II will appear strongest when the medium contains a large number of Fe^{++} atoms, and we should therefore expect the maximum of the bright recombination lines of Fe II to coincide with the maximum of the Fe III absorption lines, provided that $\rho\delta \approx \rho_0$. Unfortunately, no absorption lines of Fe III are known in stellar spectra, but from the two first ionization potentials of iron, 7.8 and 16.5 volts, we infer that our expectations are approximately confirmed. Similar arguments hold in the case of hydrogen.

We are indebted to Dr. Carl Eckart for various helpful suggestions in connection with this work and to Dr. C. T. Elvey for some of the observational material.

[28] A. S. Eddington: The Internal Constitution of the Stars, p. 382, 1926.

THE TRANSMISSION OF ELECTRONS THROUGH AN ELECTRICAL CONDENSER

By W. Wetzel
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(Received August 13, 1931)

Abstract

The formula for the transmission coefficient of electrons is calculated for a potential barrier characteristic of an ideal electrical condenser. Curves are drawn showing, for particular cases, the variation of the coefficient as a function of the condenser thickness and as a function of the final kinetic energy.

THE problem of an electron beam passing through an electrical condenser is of physical interest in that it represents one possibility of testing experimentally the incomplete transmission predicted by wave mechanics. The solution given in this paper shows that for this particular form of the potential energy function a direct test would be impossible as the conditions under which the transmission is less than unity could not be accurately reproduced in an experimental set up.

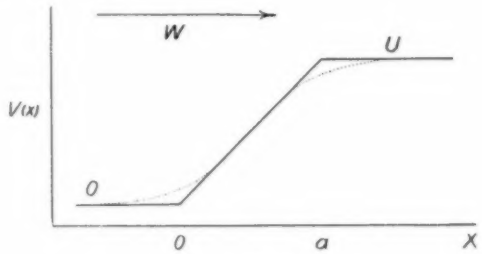

Fig. 1.

The potential barrier representing an ideal electrical condenser of width a is shown as a solid line in Fig. 1. Making use of the solution of the one dimensional wave equation

$$\psi'' + K^2(W - V(x))\psi = 0$$

given by Fowler and Nordheim, for a similar case[1] we have

$$\psi = A_1 e^{i\alpha x} + A_2 e^{-i\alpha x} \qquad x < 0$$
$$\psi = B_1 H_+(x) + B_2 H-(x) \quad 0 < x < a$$
$$\psi = Ce^{i\beta x} \qquad x > a$$

where

$$\alpha = KW^{1/2},\ \beta = K(W - U)^{1/2},\ K = \frac{2\pi}{h}(2m)^{1/2}$$

$$H \pm (x) = (y)^{1/2} J \pm \tfrac{1}{3}(\tfrac{2}{3}y^{3/2}),\ \ y = \left(\frac{Ka}{U}\right)^{2/3}\left(W - \frac{U}{a}x\right)$$

and J_n is the Bessel function of the order n.

[1] R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119**, 173 (1928).

The condition for continuity of ψ and ψ' at $x=0$ and $x=a$ results, upon elimination of A_2, B_1 and B_2, in the equation for the transmission coefficient

$$T = \left|\frac{C}{A_1}\right|^2 \frac{\beta}{\alpha}$$

$$= \frac{4\alpha\beta\left[H_+(a)H_-'(a) - H_-(a)H_+'(a)\right]^2}{\left[\alpha\beta(H_+(0)H_-(a) - H_-(0)H_+(a)) + (H_+'(0)H_-'(a) - H_-'(0)H_+'(a))\right]^2 + \quad (1)}$$

$$+ \left[\alpha(H_+(0)H_-'(a) - H_-(0)H_+'(a)) + \beta(H_+'(0)H_-'(a) - H_-'(0)H_+'(a))\right]^2$$

By use of the recurrence formula for Bessel functions[2] $xJ_{n-1}(x) = xJ_n'(x) + nJ_n$ we can show $H_-'(x) = \partial/\partial x H_-(x) = cyJ_{+2/3}(\frac{2}{3}y^{3/2})$ where $c = (KU/a)^{1/3}$ and by use of $xJ_{n+1}(x) = nJ_n(x) - xJ_n'(x)$ it is easily seen that $H_+'(x) = -cyJ_{-2/3}(\frac{2}{3}y^{3/2})$ Eq. (1) is then reducible by means of the form

$$J_n(x)J_{-n+1}(x) + J_{-n}(x)J_{n-1}(x) = \frac{2\sin n\pi}{\pi x}$$

to

$$\frac{1}{T} = \frac{1}{2} + \left(\frac{\pi Ka}{U}\right)^2 W^{3/2}(W - U)^{3/2}\{\left[J_{1/3}(z_0)J_{-1/3}(z_a) - J_{-1/3}(z_0)J_{1/3}(z_a)\right]^2$$

$$+ \left[J_{2/3}(z_0)J_{-2/3}(z_a) - J_{-2/3}(z_0)J_{2/3}(z_a)\right]^2 \quad (2)$$

$$+ \left[J_{1/3}(z_0)J_{2/3}(z_a) + J_{-1/3}(z_0)J_{-2/3}(z_a)\right]^2$$

$$+ \left[J_{1/3}(z_a)J_{2/3}(z_0) + J_{-1/3}(z_a)J_{-2/3}(z_0)\right]^2\}$$

where

$$z_0 = \frac{2}{3}\frac{Ka}{U}W^{3/2} \text{ and } z_a = \frac{2}{3}\frac{Ka}{U}(W - U)^{3/2}.$$

If we assume $z_0 \gg z_a$ we may use the asymptotic expansion for the Bessel functions of the argument z_0. Then neglecting terms of the order $1/z_0$ as small compared with unity Eq. (2) reduces to

$$\frac{1}{T} = \frac{1}{2} + \frac{\pi z_a}{6}\left[J_{-1/3}^2(z_a) + J_{1/3}^2(z_a) + J_{2/3}^2(z_a) + J_{-2/3}^2(z_a)\right.$$

$$\left. - J_{1/3}(z_a)J_{-1/3}(z_a) + J_{2/3}(z_a)J_{-2/3}(z_a)\right] \quad (3)$$

If $1/z_a$, as well as $1/z_0$, is small we may use the asymptotic expansion for z_a. Neglecting terms of the order $1/z_a$ Eq. (3) becomes

$$T = 1. \quad (4)$$

[2] For Bessel function forms see T. M. MacRobert, "Spherical Harmonics" pp. 249, 260 and 274 or any standard work on Bessel functions.

The requirement that z_0 and z_a be large (Eq. (4) valid) defines the conditions under which everyday experimental work involving electron beams is carried out. For $a=1$ cm, $U=$ a few volts and $(W-U)=$ a few volts, the conditions under which $T=1$ are satisfied.

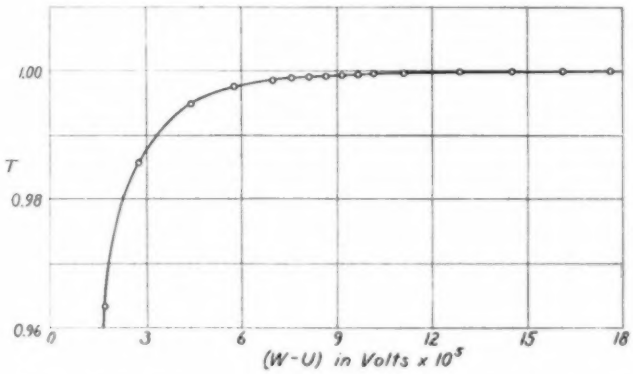

Fig. 2. Variation of T with final kinetic energy of the electron. Plotted from Eq.(3) where $U=10$ electron volts and $a=1$ cm.

Eqs. (2) and (3) could not be reduced to simpler functions. To determine the form of the transmission curves recourse was had to calculation.

If $a/U(W-U)^{3/2} \leqq 10^{-13}$ then $z_0 \gg z_a \leqq 1$ and Eq. (3) holds. A particular set of values meeting this condition is $a=1$ cm, $U=10$ volts, and $(W-U) \leqq 10^{-5}$

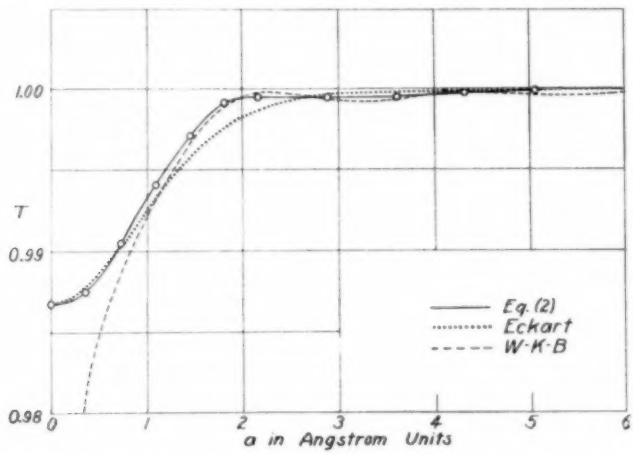

Fig. 3. Variation of T with the width of the potential rise. Plotted from Eq. (2) where $W=9$ electron volts, $U=3.3304$ electron volts. Curves of the Wentzel-Kramers-Brillouin solution for the same case and of Eckart's solution for a similar case are in good agreement with that of Eq. (2).

volts. Fig. 2 shows the variation of T with $(W-U)$. The curve increases rapidly from $T=0$ at $(W-U)=0$ to unity (within the accuracy of the calculation) at $(W-U)=1.7\times10^{-4}$ volts.

If $a \leqq 1$A $W = 9$ volts and $U = 3.3304$ volts then $z_0 \leqq z_a \leqq 1$ and Eq. (2) may be used. Fig. 3 shows the variation of T with a. Here the curve increases from the value given by wave mechanics for a discontinuous potential energy to unity at 5A. Fig. (3) shows a curve plotted from Eckart's solution for a potential energy function shown on Fig. 1 as a dotted line.[3] This is Eckart's case where $B = 0$ and l (instead of $2l$) is taken as the effective width of the potential rise. W and U are the same as those for the graph of Eq. (2). The agreement of the two curves shows that the smoothing of the potential function has little effect on the transmission. The third curve in Fig. 3 was obtained by use of the Wentzel-Kramers-Brillouin approximate solution.[4] This solution becomes zero as $a \to 0$ indicating that the approximation breaks down in high fields as well as when $W \to U$.

With the exception of the $W-K-B$ approximation the curves show no local minima. A slight depression at 3.3A in the curve calculated from Eq. (2) may exist. Its presence is supported by the minimum in the $W-K-B$ solution at that point but, as the depth of the minimum is only of the order of one in the last significant figure of the calculation, it may be due to dropped figures. When the curve of Eq. (2) was first plotted an error in the calculations gave a minimum of $T = 0.97$ at $a = 3.3$A. This led Dr. Frenkel to use the solution as a possible explanation of the selective photoelectric effect.[5] When more points were calculated to verify the presence of the minimum the error was discovered. If a minimum does exist at that point it seems to be too small to be of use in the photoelectric effect theory.

The curve of Fig. (2) illustrates very well why incomplete electronic transmission has not been detected experimentally in an apparatus of macroscopic dimensions. Velocity distribution in the incident electron beam and space charge effects would mask incomplete transmission at much higher values of the final kinetic energy than the point at which T is effectively unity.

The writer wishes to thank both Dr. J Frenkel for suggesting the problem and Dr. Max Scherberg of the Department of Mathematics for his help in its solution.

[3] Carl Eckart, Phys. Rev. **35,** 1303 (1930).
[4] N. H. Frank and L. A. Young, Phys. Rev. **38,** 80 (1931).
[5] J. Frenkel, Phys. Rev. **38,** 309 (1931).

THE VECTORIAL PHOTOELECTRIC EFFECT IN THIN FILMS OF ALKALI METALS

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(Received July 31, 1931)

Abstract

It is assumed that the photoelectric effect exhibited by thin films of alkali metals on specular platinum surfaces is proportional at any wave-length to the electric intensity just above the platinum. This electric intensity is found, using the optical constants of platinum, by computing the intensities of the wave patterns formed by the interference of the reflected and incident beams. These computations are made for various angles of incidence and for light polarized in and at right angles to the plane of incidence. The intensities thus found exhibit very large ratios of value for the two planes of polarization, in striking agreement with the characteristics of the vectorial photoelectric effect. The changes of amplitude of the perpendicular electric vector on entering the alkali metal film, as computed from the optical constants of the alkali metal, account for the experimentally found low values of the emission ratios at long, and their high values, at short wave-lengths.

WHEN polarized light falls at high angles on specular alkali metal surfaces there are markedly different photoelectric effects, depending on whether the electric vector is parallel to the plane of incidence (symbolized usually by $\parallel$) or perpendicular thereto (symbolized by $\perp$). One difference is the occurrence of the "selective" effect, or the appearance of a maximum of emission in one spectral region for $\parallel$ light, less marked or possibly absent in $\perp$ light. Another difference is one of magnitude, the photo-emission for $\parallel$ light is greater than that for $\perp$ light, *in a ratio much greater than would be predicted from the optical absorbing powers of the metal for the two conditions.*[1] These two phenomena usually go hand in hand, but for purposes of differentiation the second is sometimes called the "vectorial" effect.

The vectorial photoelectric effect is exhibited in a marked degree by the extremely thin films (circa one atom deep) of alkali metals which spontaneously deposit on clean polished platinum surfaces in highly evacuated cells having large exposed surfaces of the alkali metal. "Angle curves" for such a thin film of potassium on platinum are shown in Fig. 1, reproduced from an earlier paper.[2] In Fig. 2 are shown the absorbing power curves, plotted against angle of incidence, for both platinum and potassium, for blue light of approximately the same wave-length as that used in the experiments recorded in Fig. 1. It is to be noted, first, that the photoelectric emission curves have roughly the same shape as the absorbing power curves; thus the $\perp$ curves show in each case a slow decline in value as the angle of incidence is increased, while the $\parallel$ curves show first an increase and then a decrease, with a maxi-

[1] The occurrence of this discrepancy was adopted by Pohl and Pringsheim as a criterion for the existence of the "selective" effect.

[2] "Photoelectric Properties of Thin Films of Alkali Metals," Astrophys. J. **LX**, 4 (1924).

mum at 60° to 80°. But there is this characteristic difference, that while the ratio at 60° incidence does not exceed about 2 in the case of the absorbing powers, the ratio of photoelectric emissions rises as high as 20:1. (We have

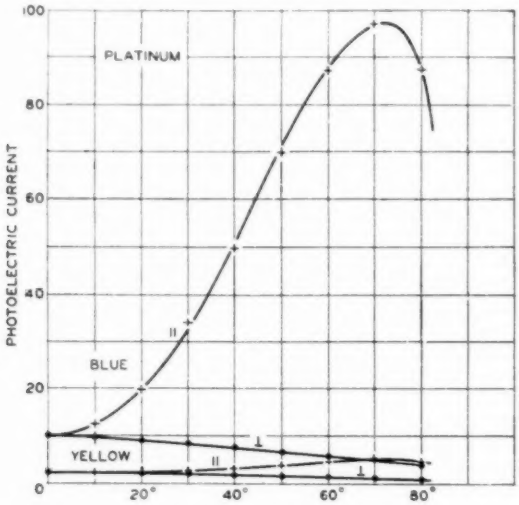

Fig. 1. Photoelectric currents from thin film of potassium on platinum for various angles of incidence, light polarized with electric vector parallel (||) and perpendicular (⊥) to plane of incidence.

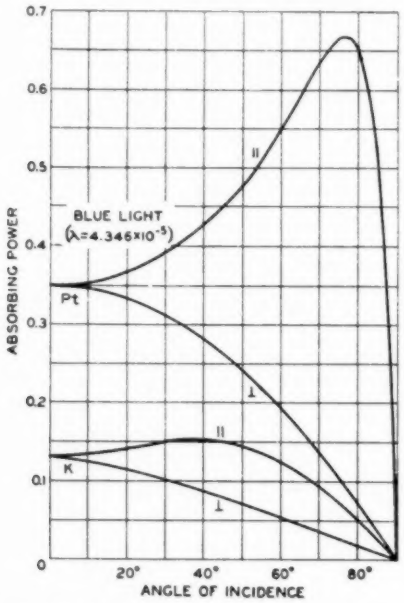

Fig. 2. Absorbing powers of platinum and potassium at various angles of incidence.

since obtained considerably larger values with carefully polished surfaces of pure noncrystalline platinum, as shown *infra*.) Now no physically possible values of the optical constants N and K_0 will give a ratio of absorbing power

at 60° incidence larger than 4. There has consequently appeared to be no quantitative correlation of the vectorial effect with the optical properties of the surface.

In some work now in progress on the photoelectric effect from thin films of alkali metal on silver, in the region of the ultraviolet where silver exhibits a band of low reflecting power (3000 to 3500A) we have found a pronounced influence of the optical properties of the silver on the photoemission. The location of the singularity in the photoemission, however, does not coincide with the minimum of reflecting power of the silver, and, in searching for the exact explanation of the effect, the clue has been found by studying the intensity of the radiant energy *at the surface* of the silver. The work on silver will be reported on later; the present paper deals with some results of applying the same line of reasoning to the photoeffect in the visible spectrum from thin films of alkali metal on platinum.

There is considerable evidence that the photoelectric effect in metals must be a phenomenon of an extremely thin surface layer. That practically as much photoemission occurs from a monatomic film of alkali metal as from the metal in bulk can be interpreted as meaning that the emission comes only from the top layer of atoms; or, the fact that electrons of the speeds characteristic of photoelectrons cannot penetrate metal layers of more than a few atoms depth may be taken as sufficient reason for restricting our attention to distances of atomic magnitude. The optical absorption is on the other hand a process requiring a distance comparable to a wave-length of light, and therefore many times an atomic diameter. If then we want to know the actual absorption of energy involved in the photoelectric effect, it is reasonable to investigate an extremely thin sheet at the metal surface.

In the case of monatomic films of alkali metal, such as potassium, on platinum, we know that the presence of the film cannot be detected by optical examination.[3] Consequently *as a first approximation* in approaching the problem we may assume that the presence of the film does not affect the condition of the light energy appreciably. Qualitatively we know that there exist above the metal surface, *standing waves*. If the metal were perfect, interference between the incident and reflected beams would produce a system of standing waves with a node at the surface, and there would be no energy for the alkali metal film to absorb. However, due to the finite conductivity of the metal, the reflected beam does not quite cancel the incident one at the planes of destructive interference, and moreover the phases are altered so that the metal surface is not a destructive or nodal plane of the pattern. Instead, there is a definite, calculable amount of enery for the photo-sensitive film to absorb. According to the view here developed a thin layer of photoelectrically active material upon a polished platinum plate takes the place of the exceedingly thin photographic layers, by means of which Wiener[4] first demonstrated

[3] "The Thickness of Spontaneously Deposited Photoelectrically Active Rubidium Films Measured Optically," J.O.S.A. **15**, 374 (1927.)

[4] Vide Woods Optics, 2d Ed., p. 174, *et sequi* for a general discussion of stationary waves in optics.

the existence of standing waves. Instead, however, of placing this film at a small angle with the metal surface, in order to get traces of successive maxima, we shall consider a sensitive film in contact with the metal surface, and shall investigate, by computation, how the light energy on the film is affected by variations of angle of incidence and of polarization. The problem thus becomes one of calculating, from electromagnetic theory, using the refractive index N, and the extinction coefficient K_0, the exact conditions just above the metal surface.

The computations of the electrical intensities in the interference pattern just above the surfaces have been made by the methods explained in a paper by Thornton C. Fry,[5] using values for the optical constants of platinum obtained by W. Meier. In the notation of that paper, when a plane wave of polarized light, whose electric vector has the amplitude E, is incident upon the plane boundary between two media, it gives rise to a reflected wave of amplitude E_2 and a refracted wave of amplitude E_1. These new beams are completely specified by the constants of Tables I and II of the paper in question. By adding E and E_2 vectorially we may obtain the amplitude of the electric force just above the reflecting surface. If we call this resultant $E_\perp$ when it is normal to the plane of incidence (and, therefore, tangent to the reflecting surface) and $E_\parallel$, when it is in the plane of incidence (and, therefore, oblique to the reflecting surface), we readily find that the former has no components in the x or z directions. Hence

$$E_\perp = E_y + E_{y2}.$$

$E_\parallel$, on the other hand, has components in the directions of x (tangential to the reflecting surface) and z (perpendicular to it), given by

$$E_{\parallel x} = E_x + E_{x2},$$
$$E_{\parallel z} = E_z + E_{z2}.$$

These equations refer to reflection from a solid substance, and give the electric force in the medium which contains the incident beam. In their application to our experiment, therefore, they give the force in the air just above the reflecting surface, when the presence of the photosensitive film is ignored. The quantities which we compute, for various angles of incidence, are $|E_\perp{}^2|$ and $|E_\parallel{}^2|$, the latter of which is defined as $|E_{\parallel x}{}^2| + |E_{\parallel z}{}^2|$. These quantities are twice the time average over a complete cycle, of the square of the magnitude of the electric force. In other words, they are twice the mean electric intensity.

There is, however, one other factor which must be taken into account. It is brought into the problem through the experimental fact that, as the angle of incidence I is varied, the size of the spot of light upon the photosensitive material increases. Hence, since the photocurrent must be proportional to the area illuminated, the values of $|E_\perp{}^2|$ and $|E_\parallel{}^2|$ must be multiplied by sec. I before a comparison with experimental data is possible.

[5] "Plane Waves of Light II," J.O.S.A. 16, 1–25 (1928).

Inspection of the full line curves of Fig. 3, embodying the results of the above computations for wave-length 4358A, shows at once that we have ob-

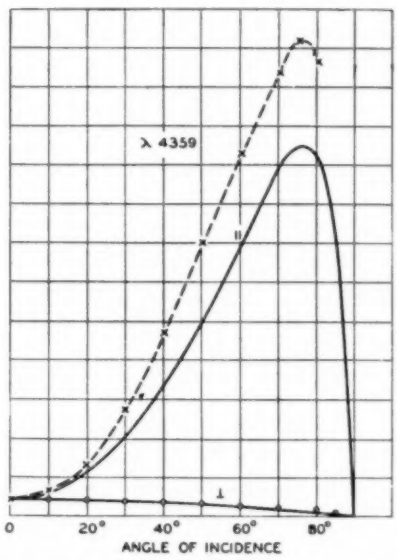

Fig. 3. Electric intensity over surface of platinum (full lines); and photoelectric currents from thin film of potassium on platinum (circles and crosses); blue light.

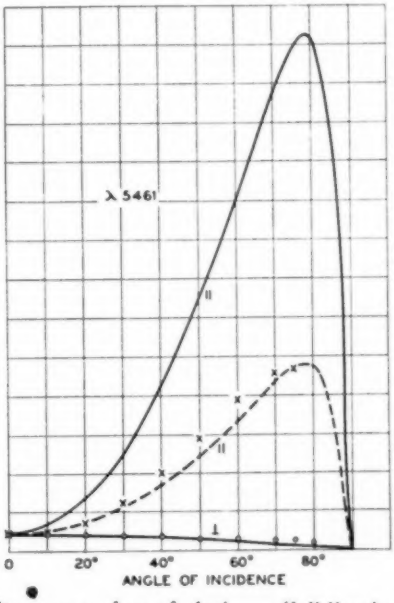

Fig. 4. Electric intensity over surface of platinum (full lines); intensity for ‖ light in thin film of potassium over platinum as computed, (dashed line); photoelectric currents from thin films of potassium on platinum (circles and crosses); green light.

tained from this line of attack what has not previously been found, an *optical* explanation of the dominant characteristics of the vectorial effect. These

angle curves exhibit a ratio of $\parallel$ to $\perp$ far greater than the ratio of the absorbing powers. For the case shown, this ratio is 29:1 at 60° angle of incidence. In the same figure are plotted recent experimental data obtained at the same wave-length, in a cell containing potassium and provided with a very highly polished plate of pure platinum (free from the microscopic dulling crystals characteristic of commerical platinum). This cell was carefully constructed so that currents from the film-covered glass walls cannot add to the photocurrents from the cathode and so yield spurious values. It is obvious that the experimental curves are closely similar to the computed, showing not only a very high ratio of $\parallel$ to $\perp$ but the same agular position of the maximum of the $\parallel$ current.

The agreement between the observed and computed curves is not exact as to magnitude, for the observed $\parallel$ curve is higher than the computed. Moreover, when we consider the computed and observed curves for green light of wave-length 5461A, shown on Fig. 4, we observe a serious discrepancy, for while the computed curves differ but little from those for blue light, the observed, in agreement with the "yellow" curves of Fig. 1, exhibit a much lower ratio between $\parallel$ and $\perp$, a phenomenon which has appeared to be general.

These discrepancies are due to the neglect, up to this point, of the effect of the alkali metal film upon the platinum. As already noted, monomolecular films (at least when deposited on metals) do not make an appreciable difference in the electric forces in the air. Hence our calculations of the standing wave amplitudes are practically unaffected by the presence of the film. However, on passing from air into the photosensitive film, while the force components in the x and y directions (tangential to the reflecting surface) are continuous, the component in the z direction is multiplied by a factor $Q = q^2/q_1^2$. In terms of the optical constants,[6] N and K_0 of the photosensitive material, this works out to be

$$Q = \frac{1}{(N + iK_0)^2}.$$

In other words, *inside* the photosensitive film the force components are given to a high degree of approximation by

$$E_\perp = E_y + E_{y2},$$
$$E_{\parallel x} = E_x + E_{x2},$$
$$E_{\parallel z} = Q(E_z + E_{z2}),$$

where the quantities E_x, E_y, E_z, E_{x2}, E_{y2}, E_{z2}, are determined without reference to the presence of the photosensitive film, and Q is independent of the nature of the material on which it is deposited.

In order to ascertain the electric intensities in the alkali metal films, Q must be derived from experimental values of N and K_0, and used as a multiplying factor on $E_{\parallel z}$, before this is used to compute.

$$|E_\parallel{}^2| = |E_{\parallel x}{}^2| + |Q^2||E_{\parallel z}{}^2|.$$

[6] For a precise definition of these constants, concerning the latter of which there is much confusion in the literature, see "Plane Waves of Light I," J.O.S.A. **15**, 137–161, (1927), especially the picture on p. 143.

In Fig. 5 are shown, first, values computed through the visible spectrum for platinum of $|E_1^2|$ sec.I, ($|E_{1x}^2| + |E_{1z}^2|$) sec θ, for $I = 60°$; and also of $|E_\perp^2|$ for perpendicular incidence. The optical constants for platinum are taken from Meier.[7] Second are shown the results of using the computations involving Q, for Na, K, Rb and Cs, taking values of the alkali metal optical constants from the literature.[8] These yield new $\parallel$ curves, the $\perp$ curves being unaffected, for they are determined solely by the underlying metal.

The curves embodying the multiplying factors show at once that the effect of the film is, in general, with all four alkali metals, to *decrease* the ratio of $\parallel$ to $\perp$ for the long wave region, and to *increase* it for the short wave region, over the ratios indicated by the platinum alone. This is in agree-

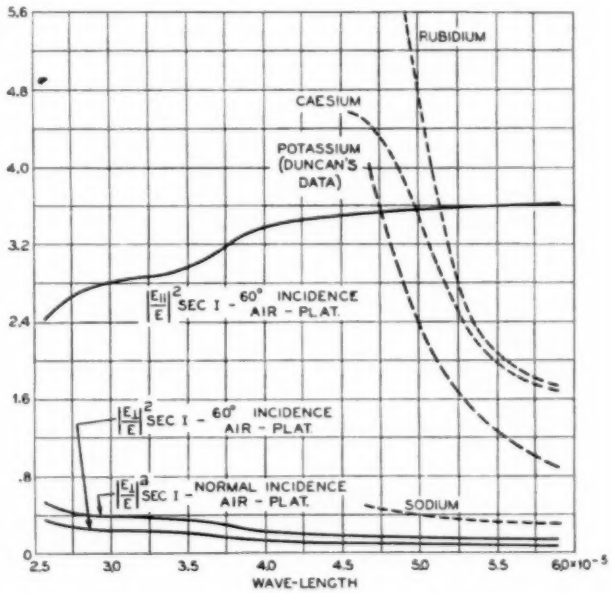

Fig. 5. Electric intensity over platinum for light incident normally, and at 60° for both planes of polarization (full lines). Intensities computed in thin films of alkali metals on platinum for $\parallel$ light (dashed lines).

ment with experiment. Furthermore it is indicated that low ratios should be obtained with sodium, and high ratios with rubidium and caesium, which is exactly what we have known experimentally for a long time.

The available data regarding the optical constants of the alkali metals are too scattering and too restricted in spectral range to be of much value for the purpose of a quantitative check. Taking, however, the potassium multiplying factor, for λ5461, which is calculated from the mean curves drawn through

[7] Ann. d. Physik, **31**, 1017 (1910).

[8] The values used were obtained by graphical averaging of data by Duncan, Nathanson and others, which exhibit considerable spread. Our own experimental determination of constants for Rb at λ5461 made in vacuo (vide note 3) differs from Nathanson's value so considerably as to suggest that a real check of the theory here presented will only be possible when all the optical constants involved are determined under the exact conditions of the photoelectric experiments.

Duncan's two sets of potassium constants, as shown in Fig. 6, the dashed curve of Fig. 4 is computed, which agrees reasonably well with the observed values. The potassium data do not extend far enough into the blue to check the λ4358 experimental curve. A straight extrapolation from the same mean data gives a ∥ curve of about twice the ordinates of the platinum curve, while the experimental potassium points lie only about 30 percent higher. It would be easy to pick an extrapolation well within the range of the experimental values of the potassium optical constants which would give an exact check, but study of this region may much better wait until more satisfactory constants are available.

As an additional check on the theory, computations have been made for the case of a thin film of rubidium on glass, previously studied experimen-

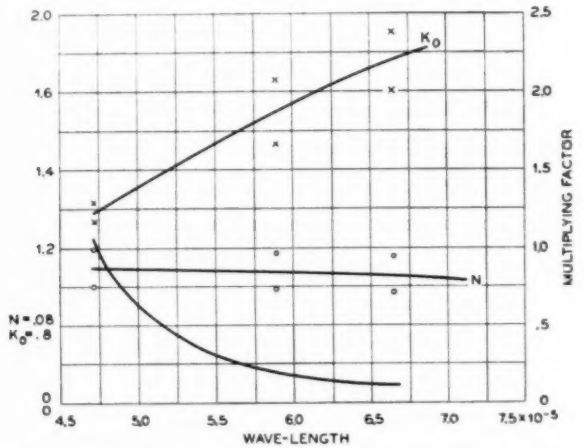

Fig. 6. Computation of multiplying factor for perpendicular light vector from optical constants of potassium.

tally.[3] The angle curves obtained (Fig. 7, dots and crosses) were quite different from those observed with films on metals, and no explanation was established. Computations of the sort here described yield the full line curves, the optical constants of the glass being taken as $N=1.51$, and $K_0=0$. By using the multiplying factor for rubidium from Fig. 5, corresponding to wave-length 4890, the dashed ∥ curve is obtained, both ∥ and ⊥ curves exhibiting close agreement with the experimental data. Actually the measurements were made for continuous spectrum light from a tungsten lamp, but in view of the predominant sensitiveness of the rubidium film for short wave energy, the "equivalent" wave-length must be somewhere in the blue, so that while the almost exact quantitative agreement shown depends upon the wave-length chosen, this wave-length is closely that which is indicated from the conditions of the experiment.

It must be pointed out in fairness that our assumption that the film of alkali metal does not affect the standing wave system formed by the underlying material is violated in the case of glass, for we have previously used the just measurable phase shift caused by the alkali metal film on glass to arrive at

the thickness of the film. However, the standing waves formed over glass have a smaller variation of amplitude than do those over metal, so that a small phase shift will alter the computed values of Fig. 7 but little.

Several points with regard to the films on platinum deserve further comment. As pointed out above, the ⊥ curves should be characteristic of the metal on which the alkali metal film is deposited. There should, therefore, be an exact check in Figs. 3 and 4 between the photocurrent angle curves observed from the thin films for ⊥ light and the electric intensity curves com-

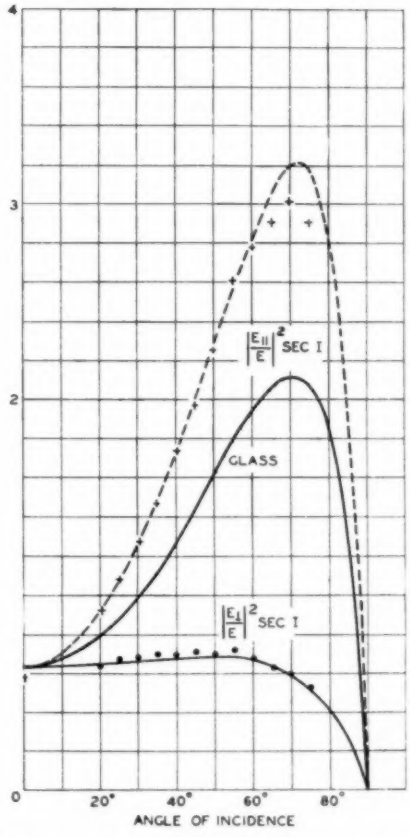

Fig. 7. Electric intensity over glass (full lines); intensity for ∥ light as computed for thin film of Rb on glass (dashed line); photoelectric currents from thin films of Rb on glass (dots and crosses).

puted for platinum. The agreement, while very close, is not, however, exact. In every case the ⊥ emission, plotted against angle of incidence, yields curves which are somewhat too flat, that is, too high at the higher angles of incidence. While this difference hardly shows on the scale to which the curves are here plotted, due to the small value of the ⊥ emission, it has been carefully checked by studies of the shapes of the ⊥ curves alone. At 60° incidence the emission should usually be only slightly greater than half that at 0°, while experimentally it approaches $\frac{2}{3}$.

The cause of this discrepancy is not yet established. It may be due to

anisotropy of the thin film, caused by an orienting of the alkali metal atoms. It may possibly lie in some small phase shift such as polishing operations are well known to produce. Inspection of plots of the standing wave amplitudes over the metal surface, shows that while the E^2 component is fairly far from a node, the E_y component is so close to a node that a very slight phase shift can produce a relatively large change of amplitude. It must, of course, be recognized that the attack on this problem through the standing wave pattern is only the first step toward a rigorous study of the actual energy absorption in the thin films without simplifying assumptions such as are here made.

Another matter may be touched on. With partially developed very thin films ($<$ one atom average thickness) the ratio of $\parallel$ to $\perp$ is much less, dropping indeed to 3:1 or 2:1 or indeed on some cases we have observed, to 1:1. One might reasonably expect this condition to be one where the standing wave system over the platinum would be least affected by the alkali metal, that is, that the values computed for platinum alone would be most closely approximated. On the other hand—and this is as far as consideration of this condition will be taken here—there is the possibility that some of the photoelectrons in this case originate in the platinum, so that the multiplying factor due to the dielectric constant of the surface will not be that computed from the alkali metal. The value of $Q=1/(N+iK_0)^2$, for platinum is much smaller than for the alkali metals, so that if the effective value of Q approximates to that for platinum as the film becomes thinner, a rapid reduction of the $\parallel$ emission would be called for, with consequent low ratios, as found.

The subject matter of this paper has been purposely confined to the *vectorial* effect, exhibited by *thin films* of alkali metal on other metals or bases. The study can obviously be extended to the distribution of photoemission through the spectrum, whereby the specific photoemission, or emission per unit of energy actually absorbed in the thin film can be determined at each wave-length. Furthermore, there is no reason to limit the application of these ideas to thin films. The bulk alkali metals and alloys can perhaps be looked upon as reflecting surfaces overlaid by photosensitive films of the same optical constants. If these overlaid films are not effectively much thicker than the films on other metals, the same treatment will apply. If they are effectively much thicker the theoretical treatment here given should serve as a useful starting point. For the extension of the study along these lines, however, it is essential that the optical constants involved be determined for the actual metal surfaces used, and the work be carried into the ultraviolet where the pure alkali metals exhibit their most marked "selective" effects. No optical constants are available for the alkali metals in the ultraviolet, so that these must be determined before the work can be carried to a satisfactory conclusion. Meanwhile it is believed the material here presented shows pretty clearly that *the vectorial photoelectric effect is predominantly an optical phenomenon.*

In conclusion I wish to acknowledge my great indebtedness to Dr. T. C. Fry for discussions of many points involved in this paper, to Miss C. L. Froelich for the computations, and Dr. H. B. Briggs for making certain of the measurements quoted.

PLASMA-ELECTRON RESONANCE, PLASMA RESONANCE AND PLASMA SHAPE

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Abstract

Plasma-electron resonance is a completely internal oscillation in a plasma and has a frequency dependent only on the electron density, whereas plasma resonance depends upon boundary conditions as well. The frequency of neither is influenced by the Debye-Hückel ion cloud. Previous theory relating plasma-resonance frequency to plasma shape is amplified and demonstrated experimentally.

I. The Distinction Between Plasma Resonance and Plasma-Electron Resonance

IN A recent paper[1] the plasma-resonance frequency was shown to be dependent upon the shape of the plasma boundary. In that article plasma-resonance was defined[2] as the actual resonance of the system comprising the plasma and the condenser of which it necessarily forms part of the dielectric. On that basis it was shown theoretically in II, section IV, that resonance occurred when $\eta' = 2$ where

$$\eta' = (1 + \theta)\eta = (1 + \theta)\omega_0^2/\omega^2,$$

and θ is the fraction of the condenser volume occupied by the plasma,

$$\omega_0 = (4\pi N e^2/m)^{1/2}, \tag{1}$$

that is, 2π times the plasma-electron frequency, and ω is the impressed angular frequency. Thus neglecting the small value of θ (about 0.056 in the actual experiments)

$$\omega = \omega_0/2^{1/2}$$

at resonance. This is the same result arrived at in II, section IX, where the natural frequency of electrons in a cylindrical plasma for parallel displacements was considered. The identity of the two results simply shows that the only function of the plane parallel condenser is to furnish a uniform electric field so that the electron displacements will be parallel.

As a consequence of these considerations the definition of plasma resonance can be generalized as the resonance of the plasma in response to a definite field configuration. The dependence of the resonant frequency on this configuration has been shown theoretically through the introduction of the shape factor, ϕ, in II, section IX, and it will be shown experimentally here.

[1] L. Tonks, Phys. Rev. **37**, 1458 (1931). This paper will be referred to as II.
[2] Reference 1, footnote 7.5.

It is important to note that any difference between the plasma-electron frequency and the plasma-resonance frequency arises from the fact that the finite extent of the plasma enters as a fundamental consideration in the latter case, whereas in the former the extent of the plasma is effectively infinite compared to the size of the oscillating region, a condition which is fulfilled whenever at every point of the plasma boundary the normal component of the electric field is zero. Under this head come the two modes of oscillation already mentioned in a previous paper,[3] namely those for which throughout a cylindrical or spherical portion of a plasma of any shape or size the electron displacements are radial and a function of radius only. It is for this case, too, that the generalized treatment in I, section I, leading to Eq. (5C) proves the independence of natural frequency and configuration.

The question naturally arises as to what significance can be attached to an oscillation which by its very nature is accompanied by no external field—what can start it and how can it be detected? Just as the thermal energy of a neutral gas may be looked upon as made up of the energy of a large number of sound waves traversing the gas, so it may be that an ionized gas possesses the additional mode of heat storage represented by plasma-electron oscillations.[4] In addition, each ionization of an atom initiates an oscillation of this type because the two electrons involved leave the scene of ionization so rapidly that in effect a positive charge has been suddenly created. Detection may well occur by means of relatively small stray fields.

The reasoning leading to I, Eq. (4), has been criticized recently by Sven Benner, "Ueber die Eigenschwingung freier Elektronen in einem Konstantem Magnetfeld," Dissert., Stockholm, May 26, 1931. He points out (p. 9) that the integration constant neglected in that derivation represents a field variable in time, although uniform in space. But he fails to note that such field would give a uniform displacement of electrons throughout the whole volume of the plasma and would, therefore, inevitably introduce boundary conditions. In addition such a displacement is inconsistent with Tonks and Langmuir's assumed nonuniform displacement throughout a portion only of the plasma. Benner's expressions for plasma resonance in cylinders and spheres are consistent with the formulas of II, section IX, and are correct if it is understood (which is not absolutely clear from the content of his paper) that parallel rather than radial electron displacements are involved.

II. The Impossibility of the Plasma Resonance Frequency being Affected by the Debye-Hückel Ion Cloud

Tonks and Langmuir have been further called to task for not including the Debye-Hückel field which arises from the ion cloud surrounding each electron and which opposes the electron motion. This field ordinarily acts as a viscous force. There is the possibility of its acting like an elastic force if in each cycle the oscillating electron encounters any remnant of the cloud

[3] L. Tonks and I. Langmuir, Phys. Rev. **33,** 195 (1929). This paper will be referred to as I.

[4] I. Langmuir, Proc. Nat. Acad. Sci. **14,** 631 (1928).

established in its previous cycle. But this is far from being a possibility, for the oscillatory velocities of the electrons must be much less than their thermal velocities to avoid local ionization effects, whence it is evident that an electron free path is only slightly undulating and any effect of the Debye-Hückel cloud must be almost exclusively viscous. Even if the electron temperature was lowered to the point where the oscillatory velocity was the larger, no elastic effect could be expected because of the way that this temperature affects the "Debye distance" also. Thus the root-mean-square electron velocity is

$$\bar{v} = (3kT_e/m)^{1/2} \tag{2}$$

Using the plasma-electron frequency

$$\nu = (Ne^2/\pi m)^{1/2} \tag{3}$$

because it is an upper limit of possible plasma-resonance frequencies, we find that the minimum net distance travelled by an electron in one period is

$$\lambda_c = \bar{v}/\nu = (3\pi kT_e/Ne^2)^{1/2}. \tag{4}$$

Finally, the "Debye distance" is

$$\lambda_D = (kT_e/8\pi Ne^2)^{1/2} \tag{5}$$

whence

$$\lambda_c/\lambda_D = 15.4 \tag{6}$$

at a minimum so that even if the cloud could have been formed in the short time available and could have persisted for the interval of one cycle, the returning electron would still be far outside its field.

III. Dependence of Plasma Resonance on Field Configuration—Experimental

The change in plasma resonance frequency arising from a change in shape factor has been observed by using an elliptical plasma between the condenser plates of the apparatus described in II and shown there in Fig. 4. A cylindrical glass tube was hand-worked to the desired elliptical cross section, was flared to circles at the ends, and was then inserted loosely in the cylindrical tube which formed an integral part of the discharge tube. This structure was used to avoid exposing the elliptical tube to the crushing effect of atmospheric pressure. The internal dimensions of the elliptical cross section were 11.7 by 26.0 mm.

Fig. 1 shows the resonance characteristics obtained for the plasma positions indicated. It will be noted that the puzzling double resonance occurs in the 0° position but not in 90° position, the slight elastic response at 20 m.a. probably arising from a small oscillation component parallel to the major axis, made possible by an inexact setting of the tube. If the a-type resonance in the 0° position be assumed to correspond to the resonance in the 90° position, it is seen that the ratio of arc currents at resonance, $17/8 = 2.1$, is very

nearly equal to the ratio of axes, $26/11.7 = 2.22$. Since II, Fig. 8, shows that ionization intensity is proportional to arc current, this constitutes a confirmation of the theory sketched roughly in II section IX and developed more completely below. The appearance of all three resonances and their unchanged positions at plasma orientations intermediate between 0° and 90° shows the independence of the two modes of oscillation, another feature brought out by the theory.

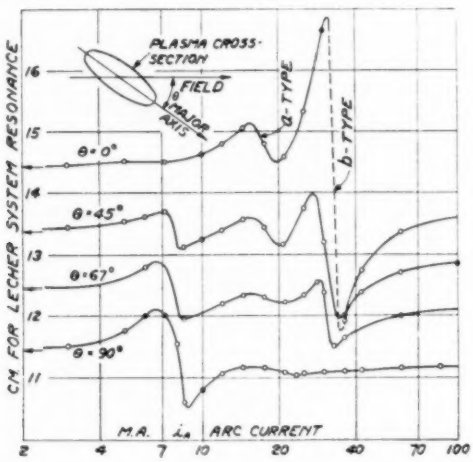

Fig. 1. Dependence of resonance in an elliptical plasma upon field orientation. Impressed frequency, 1.94×10^8 herz; condensed mercury temperature, 24 to 27°C. The zero of the ordinate scale is arbitrary, each curve being displaced 1 cm for clarity.

IV. Dependence of Plasma Resonance on Field Configuration—Theoretical

Let the x-axis of a coordinate system have the direction of the major axis, a, of an elliptic-cylindrical plasma, and the y-axis the direction of the minor axis, b, and let the impressed field $E = E_0 \sin \omega t$ make the angle θ with the x-axis as indicated in Fig. 1. Resolving the field into components, we have

$$X = E\cos\theta \quad Y = E\sin\theta. \tag{7}$$

From electrostatic theory it can be shown that if the plasma has a specific inductive capacity K_P, the electric field E_i (X_i, Y_i) inside the plasma is given by

$$X_i = X[1 + (K_p - 1)b/(a + b)]^{-1} \tag{8}$$

and likewise for Y_i. In addition, the polarization is

$$P_x = (X_i/4\pi)(K_p - 1). \tag{9}$$

Now the polarization is by definition

$$P_x = -Ne\xi \tag{10}$$

where N is the electron density and ξ the electron displacement, and the equation of motion is

$$cX_i = -m\ddot{\xi}. \tag{11}$$

Eliminating K_p, X_i, and P_x from these four equations gives

$$\ddot{\xi} + (4\pi Ne^2/m)[b/(a+b)]\xi + (e/m)X = 0 \tag{12}$$

for major axis oscillations and similarly

$$\ddot{\eta} + (4\pi Ne^2/m)[a/(a+b)]\eta + (e/m)Y = 0 \tag{13}$$

for minor axis oscillations, each independent of the other. Thus the natural frequencies corresponding to a certain electron density are less than the plasma electron frequency in the respective ratios

$$\phi_x{}^{1/2} = [b/(a+b)]^{1/2}, \quad \phi_y{}^{1/2} = [a/(a+b)]^{1/2} \tag{14}$$

where the ϕ's are the "shape factors" of II section IX.

In terms of the present experiment where N was varied to obtain resonance while ω was kept constant, we have

$$(4\pi N_x e^2/m)[b/(a+b)] = \omega^2$$
$$(4\pi N_y e^2/m)[a/(a+b)] = \omega^2$$

whence

$$N_x/N_y = a/b \tag{15}$$

as was found experimentally.

THE DIELECTRIC CONSTANT OF LIQUIDS UNDER HIGH PRESSURE

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(Received August 6, 1931)

Abstract

Values of the dielectric constant have been determined for ten liquids at two temperatures and at pressures up to 12,000 atm. except in those cases where freezing would occur at lower pressures. For chloro- and bromobenzene, eugenol, hexyl, isobutyl, and ethyl alcohol, and glycerin, the reciprocal of the Clausius-Mosotti function varies linearly with the density. Carbon disulphide, pentane, and ethyl ether, behave in a somewhat more complicated manner. The linear relations can be explained by variations of the constant of the inner field, the polarizability, or both. A theoretical discussion is given. Anomalous dispersion at 247,000 cycles was observed for eugenol, isobutyl alcohol, and glycerin.

I. Introduction

SEVERAL investigations have been made of the dielectric constant of liquids under pressure and all authors[1-9] agree that the Clausius-Mosotti function decreases. The highest pressures hitherto used were obtained by Kyropoulos[9] who subjected several liquids to pressures up to 3000 kg/cm^2. He showed that the rate of decrease of the function decreases as the pressure increases.

The apparatus available here in Professor Bridgman's laboratory made it possible to extend the investigations in this field over a pressure range four times as great as that of any prior worker. It seemed of interest to determine whether the observations of Kyropoulos would be continued at higher pressures.

Perhaps the most interesting prospect, however, was the effect on the polarization of the viscosity in those liquids where this property increases enormously under pressure. One would expect that the dielectric constant of such liquids would at first rise in the normal manner as pressure was applied. But then when high enough pressures were attained the viscous resistance encountered by the molecules would be so great as to prevent their attaining complete orientation during a half cycle of the alternating field. This phe-

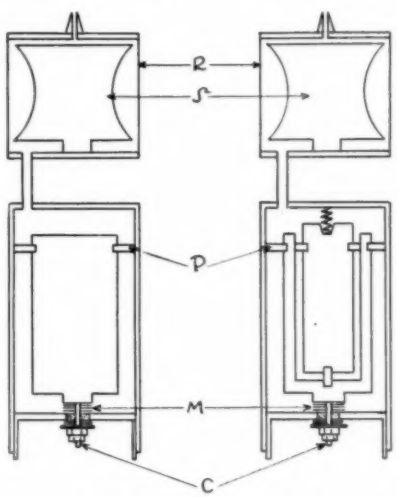
[1] Roentgen, Wied. Ann. **52,** 593 (1894).
[2] Ratz, Zeits. Phys. Chem. **36,** 1 (1895).
[3] Ortvay, Ann. d. Physik **36,** 1 (1911).
[4] Falkenberg, Ann. d. Physik **61,** 145 (1920).
[5] Waibel, Ann. d. Physik **72,** 161 (1923).
[6] Grenacher, Ann. d. Physik **77,** 138 (1925).
[7] Francke, Ann. d. Physik **77,** 159 (1925).
[8] Cagniard, Ann. de Physique **9,** 460 (1928).
[9] Kyropoulos, Zeits. f. Physik **40,** 507 (1926).

nomenon has been observed in liquids subjected to low temperatures[10–12] and its appearance at high pressures must necessarily follow if the present theoretical view is adequate. In other words, according to the theory, this form of anomalous dispersion is connected in simple manner with the viscosity and should appear when sufficiently high values of this property are produced, irrespective of the means employed.

II. Method

High pressure technique

A hand operated pump was used to produce a pressure of 1000 atmospheres which was transmitted through a glycerin and water mixture to a low-pressure chamber. There it acted upon a large piston which, in turn, pushed a



Figs. 1 and 2. The condensers. *R*, tinfoil reservoir. *P*, glass spacers. *M*, mica insulations. *C*, connection to inner cylinder.

much smaller piston into the high-pressure chamber where petroleum ether was compressed to 12,000 atmospheres.

The available motion or "stroke" of the high pressure piston was only a few inches and for compressing the required volume of liquid to 12,000 atmospheres this was inadequate. To circumvent this difficulty an auxiliary press was used which produced a pressure of 2,000 atmospheres in the high pressure chamber before the piston was forced in. This effected a large part of the total required volume reduction, and the subsequent forcing-in of the high-pressure piston produced 12,000 atmospheres without difficulty.

The measurements of pressure were made inside the high-pressure chamber to avoid any uncertainty due to friction of the piston. This was accomplished by measuring the resistance of a coil of manganin wire, a material which is known to have a linear pressure variation.

[10] Mizushima, Bull. Chem. Soc. Japan **1**, 47, 83, 115, 143, 163 (1926); Phys. Zeits. **28**, 418 (1927).
[11] Goldammer and Sack, Phys. Zeits. **31**, 225 (1930).
[12] Debye, Polar Molecules, Chemical Catalogue Co.

The measuring condensers

Figs. 1 and 2 show the design of the condensers. At the top of each is a tinfoil reservoir, both condenser and reservoir being filled with the desired liquid and sealed with solder. The whole device is placed in a steel cylinder and pressure applied through petroleum ether. The thin walls of the reservoir permit transmission of the pressure to the liquid within the condenser.

Fig. 1 represents a condenser similar with slight modifications to one used by Chang in an unpublished investigation on this subject. Its capacity was 18.4 mmf. That of Fig. 2 had the larger capacity of 35.4 mmf.

The capacity measurements

Two sets of apparatus were used for measurements of capacity at high and audible frequencies, respectively.

The audible frequency measurements were made on a Nernst bridge using a variable frequency electron tube oscillator as a source of alternating current. The test condenser was in parallel with a General Radio precision condenser in one bridge arm. Upon applicaton of pressure the increase in the capacity of the test condenser was measured by that reduction of the precision condenser necessary to restore balance.

A heterodyne substitution method was used for high frequencies. Two electron tube oscillators with frequencies of about 247,000 cycles gave an audible beat note. The frequency of one was constant and that of the other was controlled by the precision condenser having the test cell in parallel. The precision condenser was adjusted until a beat note of a given frequency was heard. The frequency of the beat note was set by comparing it with that of an audio-frequency oscillator loosely coupled to the telephone circuit. Then when the capacity of the test cell had been changed by the application of pressure the precision condenser was altered until the same beat frequency was heard.

The "air capacity" of the test cell was determined by measuring its capacity before and after filling with a liquid of known dielectric constant. Ethyl ether was used as the calibrating fluid, all determinations being made with samples taken from the same bottle. Its dielectric constant as measured in a specially designed variable condenser was 4.15 at 30°C.

Knowing the air capacity of the test condenser, the dielectric constant of a liquid at atmospheric pressure, and the capacity increase of the condenser filled with liquid when pressure was applied, the dielectric constant at that pressure could be computed.

Two easily determined corrections were necessary. One was due to elastic shortening of the condenser under pressure; the other was an extraneous capacity change introduced through compression of the lead-in insulation.

Preparation of materials

The substances studied were as follows: *Ethyl ether*—Put up by Baker Chemical Co. who had distilled it over sodium, used as received. *Carbon disulphide*—C.P. grade from Mallinckrodt, used as received. *Pentane*—Used as received from Eastman Kodak Company. *Chloro- and bromobenzene*—

Kahlbaum's purest grade, used as received. *Eugenol*—C.P. specimen put up by Merck. It had a light yellow color but no purification was attempted. *Hexyl alcohol*—This was Kahlbaum's purest grade but had a light yellow color. It was refluxed over CaO for several hours and then distilled into the condenser in dry air. The distillate was colorless. *Isobutyl alcohol*—A specimen from Eastman, distilled over CaO in a dry atmosphere. *Ethyl alcohol*—C.P. grade of "absolute" ethyl alcohol, redistilled over CaO in a dry atmosphere. *Glycerin*—C.P. specimen from Mallinckrodt, dehydrated by boiling off one third of its volume at a pressure of 3 cm.

III. Results

The data obtained for the 10 liquids described are set forth in Tables I and II and in Figs. 3–5. The variation of the dielectric constant itself with

TABLE I. *Dielectric constant and Clausius-Mosotti function (P) at high pressures.*

CS_2	p	30°			75°		
		ϵ	ρ	P	ϵ	ρ	P
Carbon disulphide	1	2.61	1.241	0.282	—	—	—
	500	2.74	1.291	.282	—	—	—
	1000	2.82	1.332	.282	2.69	1.286	0.282
	2000	2.94	1.394	.281	2.83	1.357	.281
	4000	3.11	1.487	.277	3.02	1.458	.277
	6000	3.23	1.550	.274	3.16	1.521	.274
	8000	3.33	1.601	.273	3.28	1.575	.273
	12000	3.52	1.689	.271	3.45	1.661	.271
$(C_2H_5)_2O$ Ethyl ether	1	4.15	.720	.710	—	—	—
	500	4.53	.771	.710	3.82	.709	.695
	1000	4.88	.801	.710	4.08	.740	.695
	2000	5.39	.847	.707	4.52	.797	.695
	4000	6.05	.911	.700	5.17	.866	.690
	6000	6.53	.952	.690	5.67	.906	.682
	8000	6.93	.988	.676	6.00	.941	.672
	12000	7.68	1.047	.655	6.94	.999	.655
C_5H_{12} Pentane	1	1.82	.613	.356	—	—	—
	500	1.90	.664	.354	—	—	—
	1000	1.96	.701	.352	1.92		
	2000	2.03	.743	.349	2.00		
	4000	2.12	.796	.345	2.11		
	6000	2.19	.835	.342	2.17		
	8000	2.24	.865	.340	2.22		
	12000	2.33	.907	.339	2.31		
C_6H_5Cl Chlorobenzene	1	5.41	1.004	.592	4.90	.960	.589
	500	5.59	1.038	.584	5.12	1.000	.579
	1000	5.75	1.065	.576	5.28	1.030	.571
	2000	5.98	1.105	.566	5.51	1.074	.559
	4000	6.33	1.152	.554	5.88	1.131	.547
	6000	—	—	—	6.12	1.172	.538
	8000	—	—	—	6.29	1.204	.529
C_6H_5Br Bromobenzene	1	5.22	1.465	.399	4.87	1.402	.402
	500	5.36	1.525	.389	5.05	1.461	.393
	1000	5.47	1.558	.384	5.16	1.499	.387
	2000	5.64	1.615	.376	5.34	1.560	.378
	4000	5.88	1.705	.365	5.62	1.648	.367
	6000	—	—	—	5.81	1.716	.359
	8000	—	—	—	5.95	1.762	.354

TABLE I. (*Continued*).

		30°			75°		
$C_6H_{13}OH$	p	ϵ	ρ	P	ϵ	ρ	P
	1	12.90	.812	.984	8.55	.784	.914
Hexyl alcohol	500	13.23	.839	.956	8.97	.812	.892
	1000	13.54	.861	.938	9.32	.837	.877
	2000	14.12	.894	.912	9.83	.874	.855
	4000	15.06	.937	.883	10.42	.921	.826
	6000	—	—	—	10.81	.957	.806
	8000	—	—	—	11.15	.987	.790
		0°			30°		
C_2H_5OH	1	27.8	.806	1.117	23.2	.781	1.127
Ethyl alcohol	500	28.6	.837	1.080	24.5	.816	1.088
	1000	29.4	.864	1.051	25.3	.844	1.057
	2000	30.6	.901	1.008	26.4	.884	1.014
	4000	32.5	.955	.956	28.7	.943	.959
	6000	34.0	.999	.918	30.3	.986	.932
	8000	35.3	1.031	.892	31.7	1.019	.895
	12000	37.6	1.082	.854	33.7	1.073	.857
C_4H_9OH	1	21.1	.819	1.063	17.3	.806	1.056
i-butyl alcohol	500	22.3	.854	1.022	18.1	.832	1.027
	1000	22.9	.877	.998	18.7	.856	1.004
	2000	23.8	.911	.963	19.6	.895	.969
	4000	25.0	.964	.916	20.9	.949	.925
	6000	26.0	1.001	.887	22.0	.989	.893
	8000	26.8	1.031	.864	22.8	1.018	.869
	12000	28.2	1.080	.828	23.9	1.069	.834
$C_3H_5(OH)_3$	1	49.9	1.272	.740	42.8	1.254	.744
Glycerin	500	51.0	1.292	.731	43.9	1.274	.733
	1000	51.9	1.305	.724	44.8	1.287	.728
	2000	53.5	1.330	.711	46.4	1.312	.714
	4000	56.4	1.367	.694	49.1	1.349	.698
	6000	58.9	1.398	.680	51.6	1.380	.684
	8000	61.1	1.429	.666	53.8	1.410	.671
	12000	—	—	—	57.6	1.470	.645
$C_{10}H_{12}O_2$	1	10.49	1.081	.703			
Eugenol	500	10.67	1.105	.693			
	1000	11.04	1.124	.685			
	2000	11.42	1.155	.672			
	3000	11.66	1.177	.663			

TABLE II. *Anomalous dispersion 247,000 cycles.*

Isobutyl Alcohol 0°C		Glycerin 0°C	
p	ϵ	p	ϵ
1	21.13	1	49.9
484	22.34	484	50.9
968	22.90	968	51.9
1940	23.72	1940	53.4
2900	24.38	2940	54.8
3870	24.90	3610	55.5
5810	25.90	4290	55.6
7740	26.70	4960	55.4
9490	27.26	5420	54.9
9680	27.38	6330	52.2
10100	27.30	6710	49.9
10830	27.23	7230	46.6
11290	27.00	7680	44.1
12130	26.35	8490	40.1

TABLE II. (*Continued*).

Eugenol					
0°		30°		50°	
p	ϵ	p	ϵ	p	ϵ
1	10.49	1	9.42	1	8.56
611	10.88	971	9.99	1220	9.28
1240	11.12	2080	10.48	2010	9.57
1785	11.36	2960	10.79	4040	10.20
2370	11.48	4110	11.08	6050	10.67
2550	11.53	5081	11.09	7120	10.70
2670	11.50	5400	10.90	7510	10.62
2780	11.37	5430	10.87	7540	10.49
2920	11.14	5510	10.74	8000	9.66
3030	10.91	5620	10.57	8560	8.20
3280	10.26	5800	10.10		
		6050	9.33		
		6300	6.05		

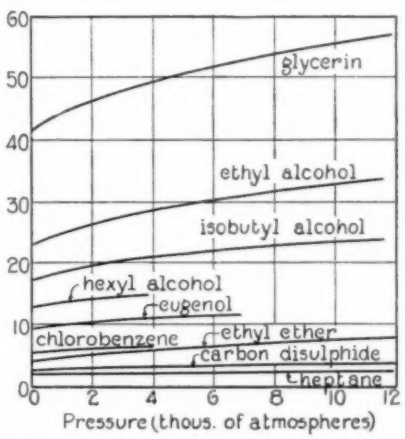


Fig. 3. Variation of dielectric constant at 30° C with pressure.

pressure is presented in Fig. 3. One sees that the curves follow the same trend as was shown in Kyropoulos's data.

The Clausius-Mosotti function (P) also continues the same general sort of variation to 12,000 atm. as was observed by Kyropoulos up to 3,000. But I found that considerable simplification appeared if the reciprocal of the function were plotted against, not the pressure, but the density. No graph of the function itself against pressure is included since I feel that the function has no molecular significance in the case of polar liquids.

Fig. 4 shows the variation of the reciprocal of the Clausius-Mosotti function with density. One observes that for all of the polar liquids except ether the curves are linear. Ether, carbon disulphide, and pentane are more complicated. It is surprising that the liquids supposedly of the more complex internal structure behave in the simpler manner.

The similarity between the slopes of the curves for different liquids is striking. The Clausius-Mosotti function usually shows greater decrease at a given pressure for liquids of higher dielectric constant, but when its reciprocal is plotted against density these differences are largely erased.

It may also be pointed out that the slope of the lower temperature curve is slightly greater in all cases.

In Fig. 5 are shown curves for the three liquids which showed anomalous dispersion at 247,000 cycles under pressure.

IV. Discussion

Since the interpretation of the above presented results is to be from a general point of view, it will be well to review briefly the fundamentals of the subject.

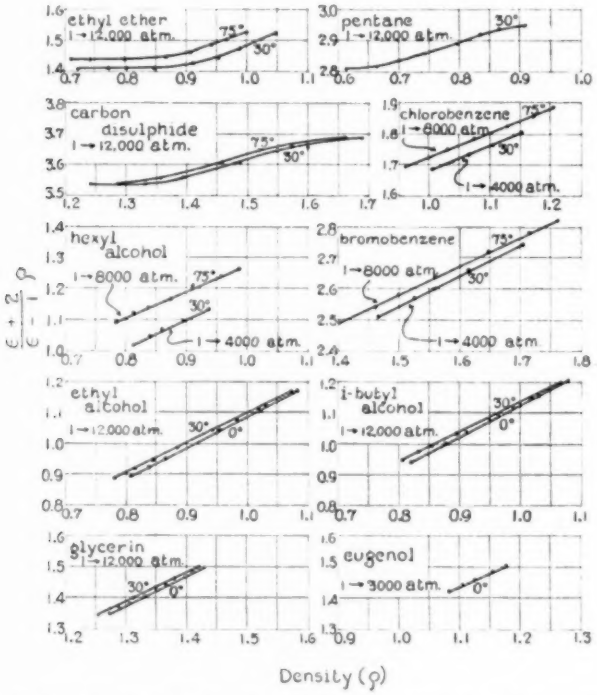


Fig. 4. Reciprocal of Clausius-Mosotti functions at high pressures.

Outline of theory

The outstanding characteristic of dielectric behavior is the direct proportionality between the dielectric polarization and the applied field. This enables one to describe the behavior of a given substance under given physical conditions by means of a single number called the dielectric constant.

In the formulation of a molecular theory for the dielectric constant expressions must be found for three fundamental processes:

(a). The way in which the applied field is modified to give the force acting on an individual molecule.

(b). The relation between this "inner force" and the moment induced in the individual molecule.

(c). The way in which the induced molecular moments combine to give the observed large-scale polarization.

It is perhaps trivial to mention item (c). The polarization per unit volume (I) of the material is simply the number of molecules per unit volume (n) times the induced electric moment (m) of each,

$$\text{i.e., } I = nm \tag{1}$$

In the expression of items (a) and (b) one may make use of the observed proportionality between the polarization and the applied field. The polarization is produced by the action of the inner field on the molecules, and the inner field is itself a function both of the applied field and of the polarization.

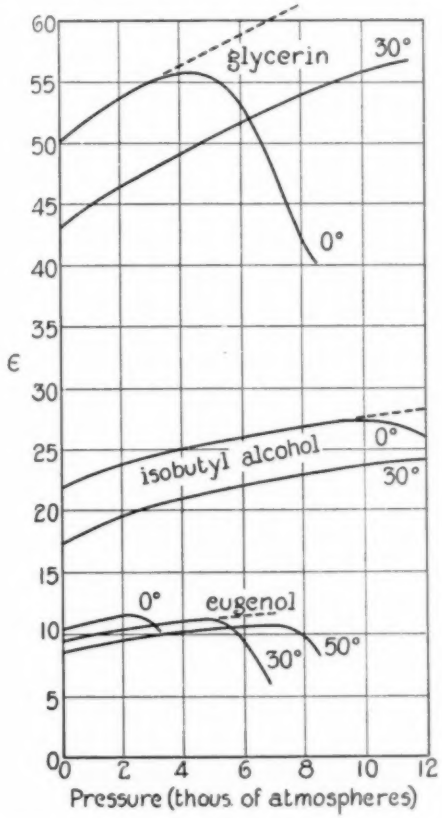


Fig. 5. Anomalous dispersion in liquids at high pressures. Solid lines, 247,000 ∽. Dotted lines 3,710 ∽.

The simplest way to describe this situation is to assume that the induced moment of a molecule is directly proportional to the inner force and that the latter is a linear function of the applied field and the polarization. One realizes, however, that linearity in both of these relations is not necessary. Deviations from linearity in the induced moment may be compensated for by oppositely-sensed deviations in the expression for the inner field, and the proportionality between polarization and the applied field may still obtain.

That such mutual compensation should exist in all of the many varieties of materials seems rather improbable. And further, modern atomic theory

looks with entire satisfaction on the notion of a linear polarizability. Hence it seems safe to assume linearity in both of these relations. One says that the induced moment (m) may be written:—

$$m = \alpha F \tag{2}$$

where α is a constant polarizability, and one writes for the inner field:

$$F = E + \nu I \tag{3}$$

where ν is the "constant of the inner field" and determines the extent to which the applied field is modified by the polarization (I).

Now from the equations of elementary electrostatics one can obtain the following quite general relation:

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{1}{\rho} = \frac{4\pi N\alpha}{3 + (4\pi - 3\nu)N\alpha\rho} \tag{4}$$

where ϵ is the dielectric constant, ρ the density, and N the number of molecules per unit mass.

This expression involves no assumptions regarding the inner field except that it varies linearly with the polarization. Its left hand side is the familiar Clausius-Mosotti function. In the usual theory the force on a molecule is assumed to be the same as if the latter were at the center of a spherical cavity in the material. One could then write $\nu = 4\pi/3$ and the above equation would reduce to:

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{1}{\rho} = \frac{4\pi}{3}N\alpha.$$

If this is true it is seen that the expression $\epsilon - 1/(\epsilon+2)\rho$ (which will hereinafter be denoted by P) is a measure of the molecular polarizability of the material. But in the case of liquids the assumption that $\nu = 4\pi/3$ is highly questionable so in general the function P has no simple molecular significance.

Interpretation of results

In a preceding section of this paper it was found that the simplest way to present the pressure variation of the dielectric constant is to plot the reciprocal of the Clausius-Mosotti function against the density.

When this is done the liquids of higher dielectric constant (chloro- and bromobenzene, hexyl, isobutyl, and ethyl alcohol, eugenol, and glycerin) give straight lines. Ether starts out horizontally and curves upward rather abruptly at about 4,000 atm. after which it seems to be fairly linear. Carbon disulphide and pentane, two nonpolar liquids, seem to start out horizontally, curve upwards, and then flatten out again at high pressures.

The decrease of the Clausius-Mosotti function P does not necessarily indicate a diminished polarizability. The above outlined theory gives us two theoretical quantities (ν and α) which may vary and account for the observations. But it may be mentioned that the decrease with increasing density may take

place without either of these quantities varying. With a constant polarizability, P will increase under pressure if ν is greater than $4\pi/3$ and decrease if it is less.

This can be seen at once if one writes the reciprocal of Eq. (4).

$$1/P = 3/4\pi N\alpha + (1 - 3\nu/4\pi)\rho. \tag{5}$$

But it also follows that α should be given by the intercept at $\rho = 0$, according to the relation,

$$1/P_0 = 3/4\pi N\alpha \tag{6}$$

and values so calculated are much larger than those measured in dilute solutions. It seems certain, therefore, that either α or ν, or both, must vary as the pressure is applied.

Unfortunately we haven't enough machinery to handle the situation if both are considered as variables. So the best we can do is to consider separately the two cases in which one is allowed to vary and the other is held constant.

(1). Let us first assume that the constant of the inner field ν is independent of the density and that the polarizability α varies. Inspection of Eq. (5) shows that the linear curves may be thus described if α follows the relation:

$$1/\alpha = 1/\alpha_0 + A\rho. \tag{7}$$

It may also be seen that A and ν, and the observed slope (m) are connected by the equation:

$$\nu = 4\pi(1 - m + A/N)/3. \tag{8}$$

This, of course, is of no value unless the constant A can be determined in some way. Knowledge of ν would permit this by means of Eq. (8), or if α were known at some value of ρ, Eq. (7) could be used. A theoretical deduction of either of these quantities would permit the evaluation of the other. But at present there seems no way out of the difficulty.

It seems highly improbable that in the case of polar liquids one can assume that $\nu = 4\pi/3$. The simplicity which this assumption lends to the equations, however, has led to its provisional acceptance in many doubtful cases. So an interpretation on this basis will not be without precedent. If this assumption is made, α can be computed directly from P. In the case of ether, α apparently decreases markedly but the difference between the curves at different temperatures seems to increase. This would mean an increasing permanent moment but a decreasing polarizability, which is inconsistent. It is also difficult to see why the value of α for the nonpolar liquids should decrease much under pressure. But the liquids whose curves are linear seem more consistent. The curves for the two temperatures seem to converge, and the decrease of the permanent moment (due to compression of the molecules or to association) calculated therefrom, is of the right order of magnitude to ac count for the decrease of P. The data are not accurate enough to verify this exactly.

(2). The alternative interpretation consists in assuming that the polarizability remains constant and that the constant of the inner field varies with the density. In some ways this seems to be the more logical method. The quantity ν is determined by the mutual arrangement of the molecules and hence seems more likely to depend on the density than does α which is more of an intrinsic molecular property.

If therefore, we let α be constant (e.g. the same as that of a molecule in dilute solution) we find that, in order to explain the observed linear curves we must let ν vary according to the relation:

$$\nu = 4\pi(1 - m)/3 + K/\rho \tag{9}$$

and it is at once apparent that since α is known and is independent of density, K can be evaluated from the intercept relation:

$$1/P_0 = 3/4\pi N\alpha - 3/4\pi K. \tag{10}$$

Data are at hand for the polarizabilities of only two of the liquids which give linear curves. Calculations carried through for these two lead to the results:

For ethyl alcohol $\nu = 0.196 + 2.07/\rho$
For chlorobenzene $\nu = 0.853 + 1.99/\rho$

It may be noted that the more highly polar of the two, ethyl alcohol, has the stronger density dependence. This is perhaps to be expected since larger permanent moment means stronger intermolecular forces and hence lends more importance to the mean distance between molecules.

Some readers might object to this interpretation on the grounds that it neglects the hypothesis of molecular association. I would point out however, that association was first brought in as a device to cover up discrepancies arising from the assumption that $\nu = 4\pi/3$. Its first application in dielectric theory was as a means of explaining the results of binary mixture experiments. The $\nu = 4\pi/3$ assumption lent a beautiful simplicity to the equations, and the association hypothesis possessed a pleasing concreteness. But it must be remembered that the observations might also have been described, and the doubtful assumption avoided, by allowing ν to vary instead of α. This is not to say that association does not exist. The rigid pairing of molecules is a logical mechansim to explain changes of α with concentration or with pressure. But such changes are always masked by variations of ν and nothing definite can be said of either until means are available to study one alone.

Anomalous dispersion at high pressures

Fig. 5 gives curves for the dielectric constant of three liquids, glycerin, isobutyl alcohol, and eugenol, measured at 247,000 cycles. Bridgman's measurements show that the viscosities of these liquids increase under pressure by an unusually large factor. They were therefore chosen as being the most promising materials for observations of anomalous dispersion.

The normal pressure effect is of course an increase in the dielectric constant. The curves rise as pressure is applied until a point is reached where the

molecular orientation begins to be suppressed by the viscous resistance. At this point the curves pass through maxima and thereafter decrease. The dotted curves show measurements at an audible frequency. The fact that they show no unusual variation proves the important point that the observed maxima are not due to freezing.

Debye's theory of anomalous dispersion in liquids[12] assumes $4\pi/3$ as the constant of the inner field and hence cannot be expected to apply to these highly polar liquids. Calculations of the molecular radii using Bridgman's viscosity data gave values considerably too small and decreasing rapidly as the viscosity was increased.

ACKNOWLEDGMENT

Without Professor P. W. Bridgman's extensive experience in high pressure research this investigation would have been quite impossible. I wish to express my thanks for his stimulating interest. I am also indebted to the Cruft Laboratory of this University for the loan of electrical apparatus.

SUPERSONIC SATELLITES AND VELOCITY

By W. H. Pielemeier
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(Received July 6, 1931)

Abstract

With increasing path length in a Pierce acoustic interferometer, minor peaks, or "satellites," were found to develop in the curves which correlate ($I_P - I_B$), *the excess of plate current over bias current*, and x, *the mirror position*. Several such curves are given. Evidence that these satellites are caused by multiple reflection is presented. The acoustic velocity as determined by these satellites, differs by less than 0.06 percent from the theoretical value, $V = (\gamma p/d)^{1/2}$, whereas the major peaks yield a velocity which, in every case, *exceeds* the theoretical value by more than 0.5 percent. Apparently the velocity approaches a limiting minimum value with decreasing *intensity*, but is independent of *frequency*.

IN A previous paper[1] the author refers to positive deviations from the theoretical value of the supersonic velocity in air. It has now been found that these deviations shrink so as to fall within the limits of uncertainty in the measurements, provided the "satellites," which are discussed in this paper, are used to compute the velocity. Since no other investigator has reported such satellites they will be discussed in some detail. The problem is that of finding their significance. The purpose of this paper is to present evidence that they are caused by higher order reflections, the waves being weakened in intensity and diminished in velocity as they travel back and forth. A further purpose is to determine the minimum velocity at each frequency and to demonstrate a variation in velocity with *intensity*. A test as to whether the *minimum* value of the velocity varies with *frequency* is also involved.

The general method of the investigation is the same as that used previously by the author[2] except that a careful study of the satellites is added. With this exception similar work has been reported by G. W. Pierce,[3] Charles D. Reid,[4] J. C. Hubbard,[5] E. Klein and W. D. Hershberger[6] and others.

Apparatus

Quartz piezoelectric oscillators were used as sources. Some of these were sputtered with platinum and others with silver. The metal films serve as electrodes which are forced to oscillate with the same amplitude as that of the quartz surface. Thus a sound beam is radiated from the largest face of each crystal. The ratio of face area to the acoustic wave-length is large enough to insure approximately parallel sound beams. In the least favorable case the diagonal of the square radiating surface was 53 mm and the wave-length was

[1] W. H. Pielemeier, Phys. Rev. **36,** 1005 (1930).
[2] W. H. Pielemeier, Phys. Rev. **34,** 1184 (1929).
[3] G. W. Pierce, Proc. Am. Acad. Arts and Sciences **60,** 271 (1925).
[4] Charles D. Reid, Phys. Rev. **35,** 814 (1930) and **37,** 1147 (1931).
[5] J. C. Hubbard, Phys. Rev. **36,** 1688 (1930).
[6] E. Klein and W. D. Hershberger, Phys. Rev. **37,** 633 (1931).

1.09 mm. This results in an angle of about three degrees to which the central beam of the diffraction pattern is confined. With such a narrow beam and the rather short path lengths there are many reflections back and forth before the wave intensity becomes negligible on account of the spreading wave front. The crystals were operated in a UX-201-A vacuum tube circuit. A hair hygrometer was kept in the cast iron air chamber. The humidity was kept low with $CaCl_2$. Some tests were made with a padded mirror, the intention being to diminish the number of reflections. The mechanical backlash in the micrometer screw was measured by focussing a microscope on a sharp edge of the plate glass reflector. Some of the crystal frequencies were checked by means of standard crystals at the college broadcasting station, WPSC, and by the incoming waves from other stations.

RESULTS

The results are presented in the form of curves and tables. The curves, Figs. 1 to 4, show the excess of plate current over the galvanometer bias current, $(I_P - I_B)$, as ordinates and the mirror positions, x, as abscissas.

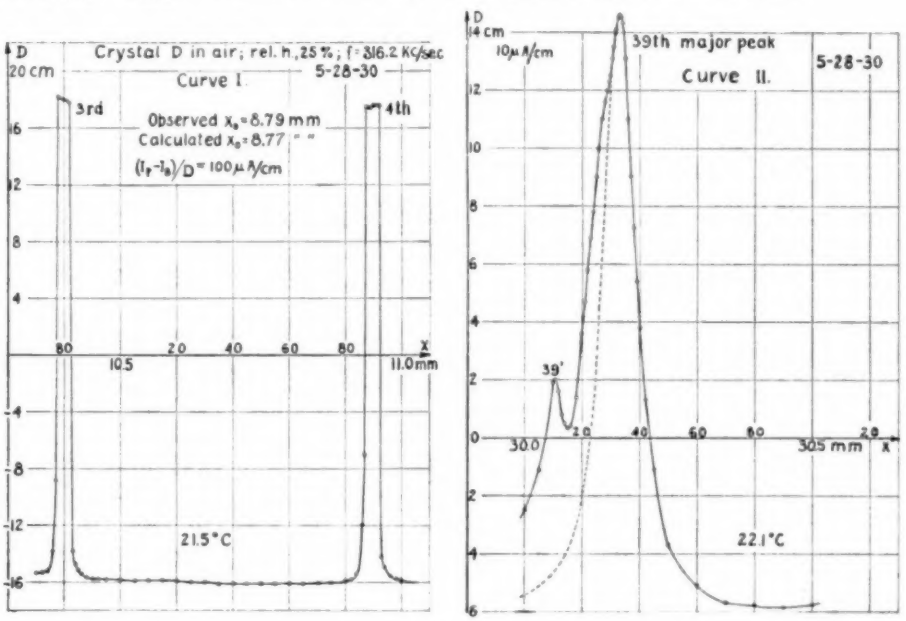


Fig. 1.

Reid[4] reports a peak displacement which might be termed an "*acoustic* backlash." Such a backlash was observed with the lower frequencies listed in Table I. The largest observed backlash was less than 0.02 mm (approximately $3\frac{1}{2}$ screw divisions). If there was any acoustic backlash with the *highest* frequency it was less than 0.005 mm. Near the tenth peak it appears to be roughly 0.01λ at each frequency. It is found by subtracting the *mechanical* backlash from the *total* backlash as indicated by the peaks when the screw is reversed.

The same type of curve was obtained with metal blocks of different thickness under a *given* crystal. For two *different* crystals the peak patterns are dif-

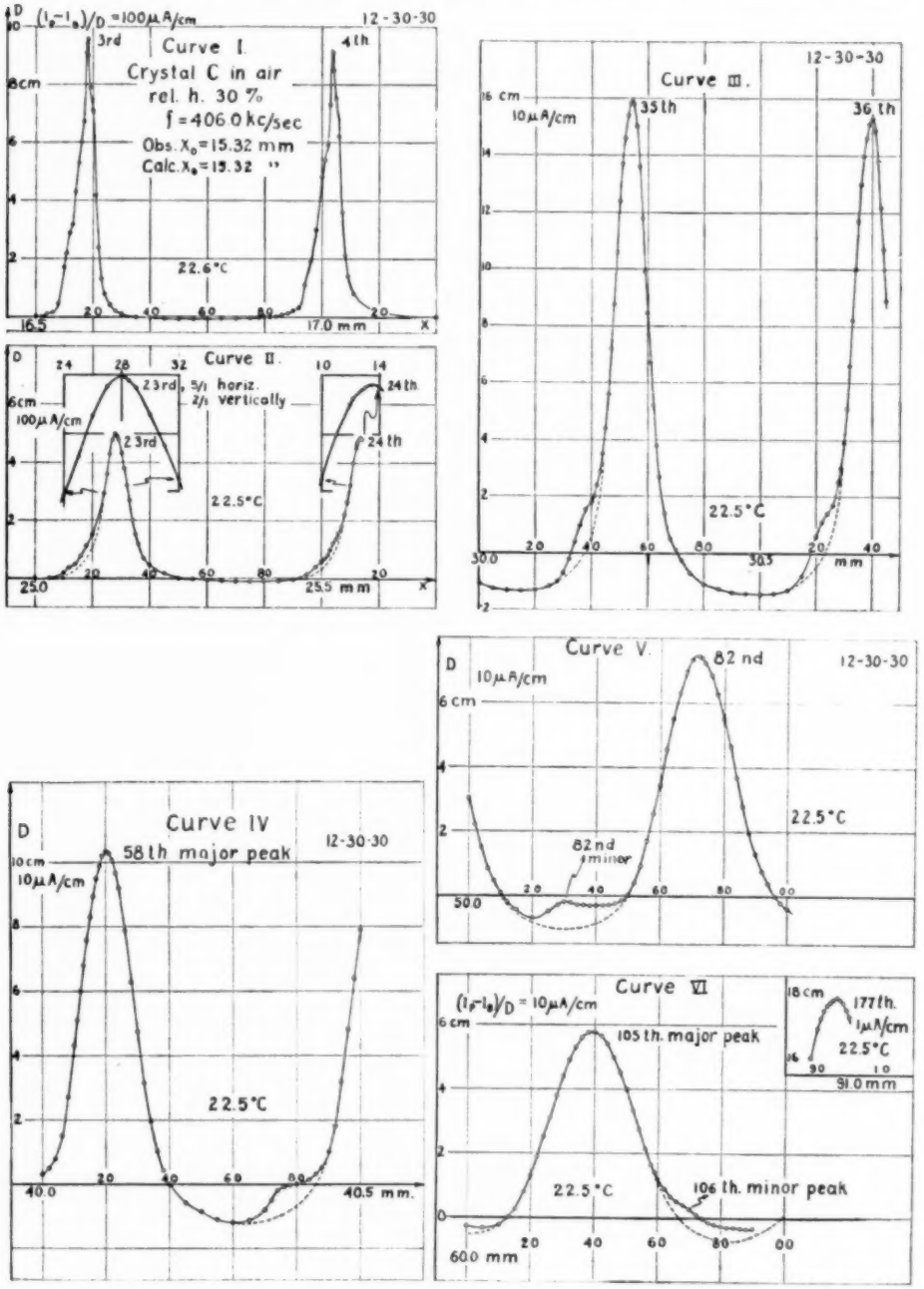


Fig. 2.

ferent for the same portion of the screw. These facts indicate that the screw is not the cause of the peculiarities of the curve.

TABLE I.

f Kilocycles	t °C	h %	V_t m/sec.	V_0 m/sec.	V_0' m/sec.	Date
316.2	26.8	29	347.8	331.7	334.2	5–21–30
316.2	21.6	25	344.5	331.6	333.9	5–28–30
389.3	19.5	*20	343.3	331.65	333.6	3–27–30
389.3	25.6	19	347.0	331.6	333.8	7–11–30
406.0	22.5	30	345.1	331.6	333.6	12–30–30
406.0	22.5	28	345.1	331.6	333.5	1– 9–31
655.5	25.7	30	346.9	331.5	333.9	2–18–31
647.9	26.8	26	347.7	331.6	333.4	4–15–31
647.9	24.6	25	346.3	331.6	333.3	4–15–31
1216.	19.8	31	343.5	331.7	333.3	10–29–30
1216.	27.4	34	348.0	331.6	333.2	4–17–31
1216.	25.9	23	347.3	331.6	333.1	5–14–31

NOTE: f = frequency; t = temperature; h = humidity; V_t = velocity at t°C and V_0 = velocity at 0°C determined by the satellites. V_0' = velocity at 0°C determined by main peaks.
* estimated.

DISCUSSION OF RESULTS

The work of Reid[4] and Hubbard[5] indicates that there is no variation of velocity with frequency, in other words, that acoustic dispersion does not exist. The same may be said of the satellite data presented in Table I. From these satellite data a limiting (minimum) velocity is calculated for each frequency. This velocity differs by less than 0.06 percent from the theoretical value, $V = (\gamma p/d)^{1/2}$. This difference is just within the limits of uncertainty in the measurements. There is no noticeable change in spacing of these satellites with increasing mirror displacement such as that observed by the writer and by Reid[4] in connection with the ordinary peaks. However, with an im-

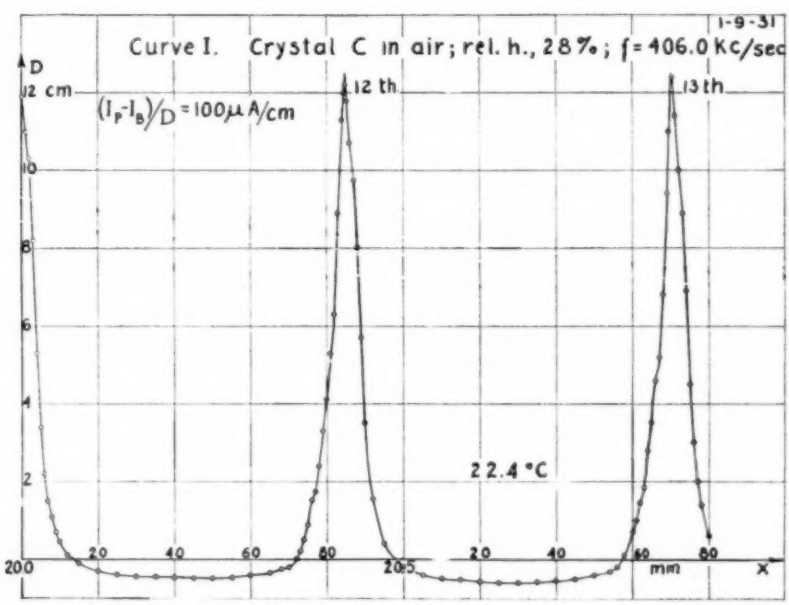


Fig. 3.

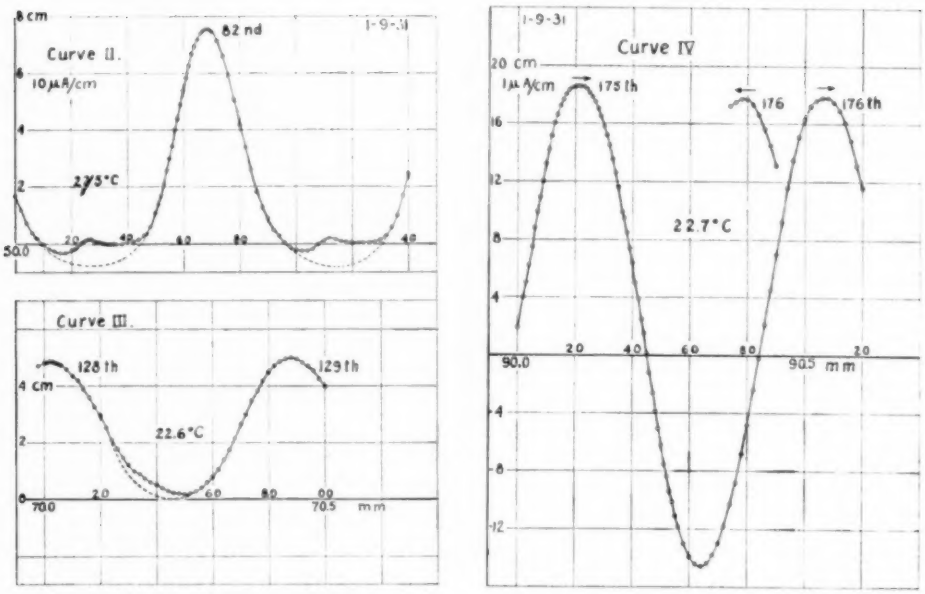


Fig. 3 (*Continued*).

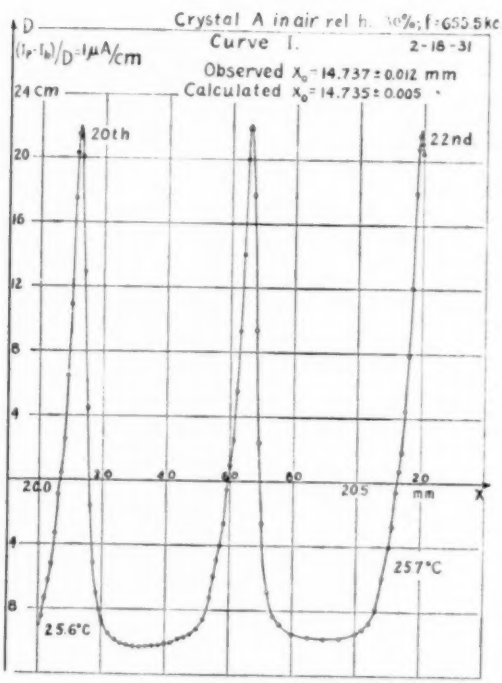
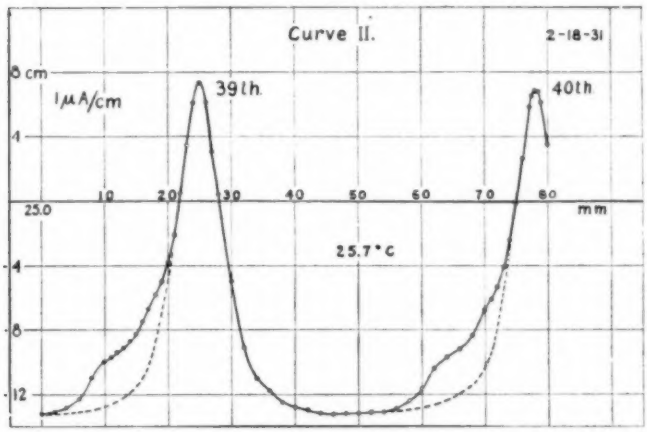
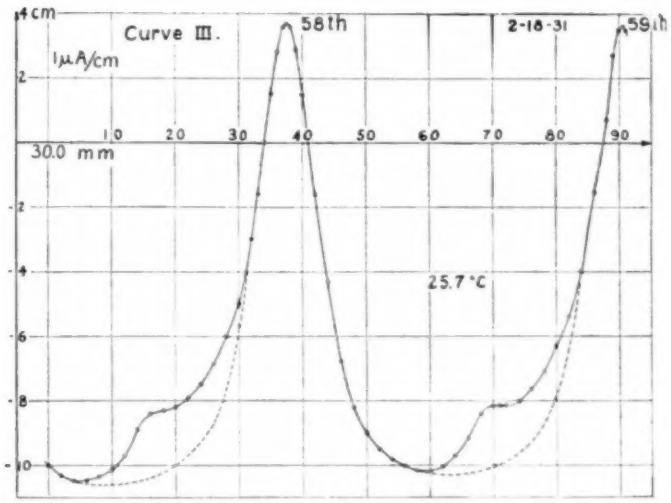


Fig. 4.





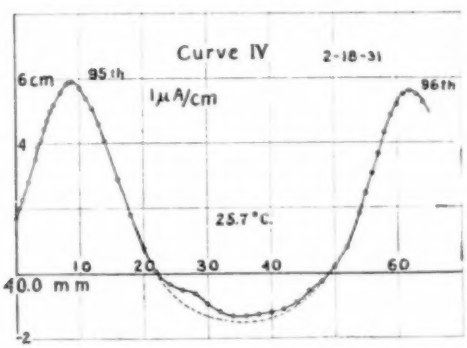


FIG. 4 (*Continued*).

proved method of holding the frequency constant, Hubbard[5] reports a *constant* spacing of the ordinary peaks. If the emitted intensity was quite low, this would be expected. Neither he nor Reid reported satellites accompanying the main peaks. In the latter case this might have been due to the rapid spread of the beam at the rather large wave-lengths used. If the author's main peak data are used, a velocity is obtained, which, in every case, *exceeds* the theoretical value by more than 0.5 percent and in some cases by more than 1.0 percent. The spacing of the *major* peaks varies with increasing mirror position as observed by Reid.[4]

The curves obtained with a padded mirror showed a slightly smaller peak spacing and there was very little tendency to form satellites. A padded mirror reflection causes a large reduction in intensity and the first return trip is probably the only effective one for all except very short path lengths.

It is not difficult to follow the satellite system through the curves of Figs. 1 to 4. The progressive lagging of the satellites behind their major peaks is one of the most striking features of these curves. At the third and fourth resonance positions shown in Fig. 1 the reaction on the crystal was sufficient to stop the oscillations as was verified by keeping the plate voltage and filament current at their ordinary value and stopping the oscillations by pressing the crystal with a rubber pad. At once I_P rose to the level of the truncated peaks, although the mirror was set between two resonance positions. The twelfth peak (not shown) had a tendency toward a satellite at the left base. As shown in curve II, the 39th peak has a pronounced satellite, and a secondary maximum almost merges with the main peak. The dotted lines in these figures make the major peaks symmetrical and form an estimated base for the satellites. Readings were taken for major peak and satellite positions extending out to much greater mirror displacements. It was found that the lag persisted until it reached a half wave-length or more where the satellites were so weak that they could not be located very definitely.

In Curve I, Fig. 2, individual responses to the first few returns to the crystal are evident in each peak. The insets in curve II show parts of the 23rd and 24th peaks magnified. The smallest attempted increase in x was 0.001 mm ($\frac{1}{5}$ screw head division). Definite satellites have developed in curve III. The progressive space lag is shown in curves IV, V, and VI. Curve II of Fig. 3 represents an excellent check on the data of curve V, Fig. 2.

Incomplete satellite data for oxygen indicate that the limiting velocity at 0°C is approximately 314.8 m/sec, which is also the theoretical value. The value computed from the main peaks is given in an earlier paper[1] as approximately 317.4 m/sec.

Since no other observer has reported the presence of "acoustic satellites" a few hypotheses as to their cause will now be presented.

1. The crystal may continue to vibrate at its natural frequency until the mirror reaches such a position as to produce resonance to a slight degree and therefore a sufficient added load, or reaction, might thereby be applied to the vibrating crystal to suddenly diminish its frequency and thus cause a slight drop in the plate current. As the mirror displacement increases the frequency

might approach its lower limit thus making the crystal more capable to withstand the increased load caused by better resonance; i.e. by the phase coincidence of the emitted waves and those completing the *first* trip. Thus the mirror, passing through the best resonance position, would produce a major peak. Slightly greater displacements would produce large drops in plate current. This would partially account for the shape of the curves.

The objection to this explanation is that the necessary load for such a large frequency shift would stop the oscillations entirely. Reid[4] apparently failed to observe a noticeable frequency shift as a resonance position is approached.

A *small* frequency shift of this kind might account for the acoustic backlash, however. It might also slightly modify the shape of the major peaks. Such a frequency shift is referred to in the German literature on coupled electric circuits as "Ziehen und Reissen."

2. The satellites may be caused by a phase lag of certain parts of the crystal surface behind the rest resulting in a sort of rotating *surface* wave and causing the emitted *sound* wave fronts and the crystal surface to be nonparallel.

If this were the case it should be possible to adjust the tilt of the crystal so as to eliminate the satellites. It was found that in some cases an extremely slight adjustment following a visual one caused the major peaks to become more sharp and narrow for a range of mirror positions from 1.5 to 10 mm from the crystal. Apparently this had no effect on the true satellites which could scarcely be distinguished from the first few peaks. Moreover, the curves show a progressive lag of the satellites behind their major peaks of just the right magnitude to give the theoretical velocity ($V_0 = 331.6$ m/sec). By the above hypothesis this would scarcely be possible.

3. The presence of overtones may account for the satellites.

It would be very remarkable if the crystal were to perform so as to make the satellites, instead of the *main peaks*, on this hypothesis give the accepted velocity. The frequency of one of the crystals was obtained more precisely by beats with a standard crystal at station WPSC. Then the frequency was computed from the constant satellite spacing and the accepted velocity of audible sound. These two values for the frequency differed by less than 0.02 percent.

4. The satellites and the other deviations from symmetry in the main peaks may be caused by a gradual increase of velocity above the lower limit, $V = (\gamma p/d)^{1/2}$, as the intensity approaches that of the waves when they are first emitted. This *maximum* velocity would be somewhat greater than the value obtained from the major peak spacing.

This explanation is proposed by the writer as the correct one. The strongest evidence against the others becomes the best evidence in favor of this one; namely, that the uniform spacing of the satellites gives the accepted velocity of sound. Moreover, the other deviations from symmetry in the main peaks, and their excessive spacing are explained by it. Then the satellites do not represent a separate *frequency* as in spectroscopy but, rather a limiting *velocity* at the *one* existing frequency.

In an earlier article[1] it is shown that the maxima of the $(I_P - I_B)$ curves appear at the same mirror positions as do the maxima of pressure amplitude in the air at the crystal surface. Fig. 5 shows how the square of the pressure amplitude varies with mirror displacement, assuming constant wave velocity and perfect reflections at the mirror and also at the vibrating crystal.

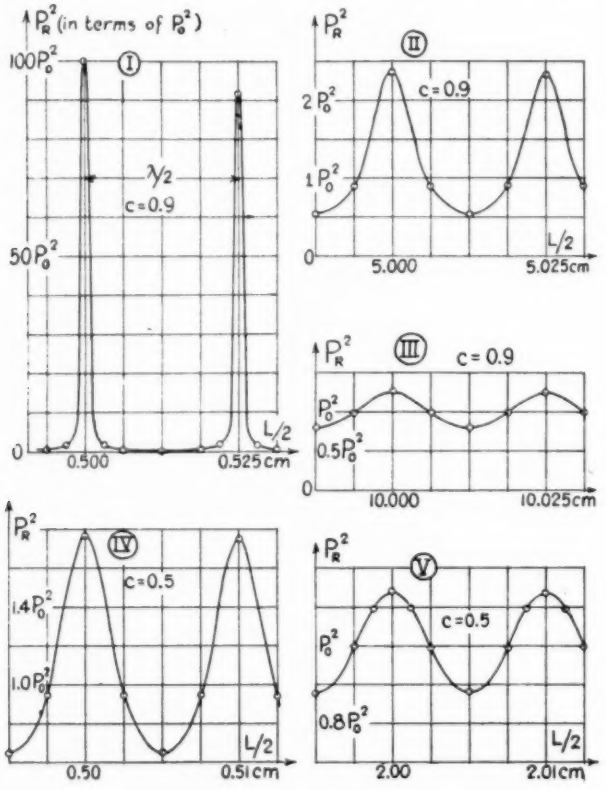


Fig. 5.

The points for this curve were obtained from the equation

$$(P_R)^2 = \left[\sum_0^n P_0 c^{nL} \cos(-\omega nL/V) \right]^2 + \left[\sum_0^n P_0 c^{nL} \sin(-\omega nL/V) \right]^2 \quad (1)$$

in which P_R represents the *resultant* pressure amplitude at the crystal,

P_0, the pressure amplitude due to the *emitted* waves only.

n, the number of return trips made by the wave train.

c, the fraction of P_0 left at the end of the first unit of path length.

L, the length of one return trip.

V, the wave velocity (assumed constant in this equation).

$= 2\pi f$, where f is the frequency of the crystal

$-(\omega nL/V)$ = the phase angle for the returning waves as they are being reflected the nth time by the crystal.

$L = 2(x - x_0)$ where x_0 is the crystal position.

It may be seen from Eq. (1) that a variable wave velocity, V, will prevent perfect resonance. In other words, there will be no position of the mirror which will cause *all* the reflections at the crystal to differ in phase by a whole number of periods. The higher order reflections will require a shorter path (smaller mirror displacement) to bring them into phase coincidence with the emitted waves. If the reflections at the vibrating crystal were equally good for all phases of arrival in the returning wave trains there would probably be no satellites but rather a more gentle slope without minor peaks on the left side of each major peak. If, however, the absorption in a single return trip should reduce the intensity, and hence the velocity sufficiently, there might appear separate humps for each return trip until the limiting velocity is reached. The linear separation of such humps would depend on the path length as well as on the velocity range. Very probably, however, the reflecting power of the crystal depends decidedly on the phase at arrival. A condensation, returning to be reflected, will be largely absorbed and will feed energy into the crystal momentarily, if the crystal is contracting and therefore emitting a rarefaction at that instant. If the path length or the velocity change is great enough to produce a linear separation of the humps of more than a small fraction of one half wave-length, there will be a great reduction in the reflecting power of the vibrating crystal and the humps will fail to appear. When the mirror displacement is a little less than that required for a major peak (e.g. where the first hump might be expected) the path length is too short for resonance with respect to the first return trip. Consequently the intensity and velocity will be greatly reduced so that the mirror would need to be moved nearer the crystal to make the second return arrive in phase. But this will accentuate the reduction at the first reflection. Thus there is a strong tendency for a shift toward low intensity and the limiting velocity in all except the first return trip. Curve I, Fig. 2, shows several humps at small linear separation due to a short path length. When the mirror is at a resonance position for the waves which have reached the limiting velocity all the succeeding reflections will be in phase and a small peak is produced by the cumulative effect of all of them, there being little reduction in intensity due to the successive reflections after the limiting velocity is reached. A further decrease in intensity would merely affect the height but not the position. Sudden changes in the logarithmic decrement of peak height for the smaller mirror displacements also suggest the breaking away and disappearance of humps in the major peaks. The logarithmic decrement of the peaks in Fig. 5 (constant V) changes with L but there are no *sudden* changes. The minor peaks caused by the waves which have reached the *limiting* velocity are considered as the true satellites. This exludes the other humps and the minor peaks caused by lack of proper mirror alignment. A careful study of Figs. 1–4, with the above explanation in mind, is rather convincing.

A decrease in wave-length and therefore in velocity with diminishing intensity for audible sound was observed by H. O. Taylor.[7] Hitchcock[8] made

[7] H. O. Taylor, Phys. Rev. **32,** 270 (1913).

[8] R. C. Hitchcock, Proc. Inst. R. E. **15,** 907 (1927).

similar observations on ultrasonic waves from crystals. Theory predicts such a variation, at least for the condensations.

Probably other investigators have failed to observe satellites because their sound beams diverged so fast that the second reflection contributed a negligible amount to the intensity. This would hardly explain Hubbard's[5] constant spacing unless the waves were *emitted* at low intensity and practically the limiting velocity.

Since there is no apparent dispersion of low intensity sound waves in air the Pierce acoustic interferometer may be used not only to measure supersonic velocities in other gases using known frequencies, but also to measure the frequency of crystals to four or five significant figures if the gas is air and if the sound intensity is known to be sufficiently low.

Gas densities are usually given for so-called standard conditions. The pressure, however, is not definite unless it is given in absolute units. Unfortunately it is not customary to state the pressure in absolute units nor to give the corresponding gravitational field intensity in connection with gas density tables. In order to compute the velocity of sound to the nearest 0.1 m/sec by the formula, $V=(\gamma p/d)^{1/2}$ the mere statement, $p=760.0$ mm of mercury, is, of course, insufficient. (Probably the best computed value and also the experimental value for low intensity sound is 331.6 m/sec at 0°C.

The data presented in this paper may have some bearing on the theory of standing waves and in some cases on the sharpness of resonance.

AN INTERCOMPARISON OF THE HIGH TEMPERATURE SCALE

By W. E. Forsythe
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(Received July 23, 1931)

Abstract

List of laboratories taking part in intercomparison.—This paper gives results on an intercomparison of the high temperature scales in use at the Physikalisch-Technischen Reichsanstalt in Berlin, the Laboratoire Central in Paris, the Laboratory of the Philips Glowlampworks in Eindhoven, and the Laboratory of the Osram Lamp Company at Berlin with that in use in the Laboratory at Nela Park. For purpose in comparison the results of a previous intercomparison with the Bureau of Standards, the National Physical Laboratory at London, the General Electric Research Laboratory at Schenectady, and the Physical Laboratory at the University of Wisconsin are included.

Method of comparison.—Several tungsten lamps that had been carefully aged and calibrated were sent to each of the foregoing laboratories and the temperatures of the lamps were measured for specified currents with a disappearing filament optical pyrometer using red glass as the monochromatic screen. The reductions necessary to make the readings comparable because a nonblack body was used are pointed out. Results of the first intercomparison are given in Table II and the final intercomparison given in Table III. Very good agreement was found in this intercomparison, the maximum difference being only a few degrees for any point of the entire range from about 1400 to 2700°K.

SEVERAL years ago an intercomparison[1] of the high temperature scale in use in the Laboratory at Nela Park was made with that in use at the Bureau of Standards, the National Physical Laboratory of England, the General Electric Research Laboratory at Schenectady, and the Physics Laboratory at the University of Wisconsin. This intercomparison was made by measuring the brightness temperature of a number of special tungsten filament lamps that had been prepared and calibrated at Nela Park and then sent to the different laboratories.

In Figure 1 is shown a picture of one of each type of lamp used in the intercomparison and in Table I a description of the different individual lamps is given.

The exact point at which the temperature of each of the ribbon lamps was to be measured was indicated either by a pointer, a notch in the supporting lead, or a small notch in the ribbon itself. The wire filaments of the other lamps were in the form of a hairpin loop with a rather sharp bend. The temperature of these filaments was measured at the center of the loop. Very good agreement was obtained by the laboratories that took part in this earlier work, as can be seen from the data which are given in Table II for the purpose of comparison.

The intercomparison has now been extended, by measurements on the

[1] Astrophys. J. 58, 294 (1923).

same type of lamp, to include the Physikalisch-Technischen Reichsanstalt of Berlin, the Laboratoire Centrale of Paris, the Laboratory of the Philips Glowlampworks in Eindhoven, Holland, and the Laboratory of the Osram Lamp Works at Berlin.

Fig. 1. Picture of one of each of the different types of lamps used in the intercomparison. Numbers 1 and 3 have ribbon filaments; number 2 has a 20-mil. (0.5 mm) diameter wire filament.

The high temperature scale is, in general, based upon the brightness of a black body at the temperature of melting gold taken as 1336°K. Since the extrapolation is made by means of Wien's equation the best value for C_2 must be agreed upon. The value accepted by the International Critical Tables was 14326 μ deg. Recently the International Conference of Weights and Measures adopted the value of $C_2 = 14320\ \mu$ deg. for pyrometric measurements. To be in keeping with this value all values of temperature in this paper should be increased by about one degree at 2000 and two degrees at 2700°K. This change would thus not affect the agreement obtained.

The brightness temperatures of the lamp filaments were measured in each

TABLE I. *Description of the lamps used in the intercomparison.*

Lamp No.	Kind of filament
T-25-C	Horizontal ribbon, 2.5 mm wide, gas-filled.
T-17-C	Horizontal ribbon, 3 mm wide, gas-filled.
T-16-B, F-75-C, F-76-C, T-18-B, F-71-C, F-74-C, F-116-C, F-117-C	Vertical ribbon, 2.5 mm wide, vacuum.
T-30-C, T-77-B, T-78-C, 181–184, F-114-C, F-115-C	Wire, 20 mil (0.5 mm) diameter, gas-filled.

laboratory with a calibrated disappearing filament optical pyrometer. Monochromatic radiation was obtained in each case by using a piece of red glass in the eyepiece of the pyrometer. As is well known an optical pyrometer can be calibrated[2] over a wide range of temperatures without a knowledge of the effective wave-length[3] of the radiation used providing the proper precautions are taken. In general, however, the means used to extend the scale to high temperatures requires a knowledge of the effective wave-length of the screen used. If the optical pyrometer is used to measure the temperature of a nonblack body[4] the effective wave-length must be known as is shown in what follows.

In using the optical pyrometer it is the integral-luminosities through the glass screen that are compared and for this reason the effective wave-length[3] of the glass screen for a certain temperature interval has been defined as the wave-length such that for a definite temperature interval for a black body the ratio of the radiation intensity for this wave-length shall equal the ratios of the integraluminosities through the screen used. The effective wave-length of a glass screen is not constant but varies for different temperatures.

To make certain that the different laboratories agreed in their determination of the effective wave-length a pair of red glass screens were carefully calibrated at Nela Park for effective wave-lengths and sent to a number of other laboratories for their determination of the effective wave-length of the screen. Either the same pair or a pair cut from the same sample were sent to the different laboratories. The laboratories that made such determinations (National Physical Laboratory, Physikalisch-Technischen Reichsanstalt, and the Laboratory of the Philips Glowlampworks) agreed in their determinations to about one or two parts in six thousand.

Although these intercomparisons have been carried out by measurements on tungsten filaments the results give not only the comparisons of brightness temperature of the tungsten filaments but also a valid comparison of the high temperature scale as determined from the standard black body. If strictly monochromatic radiation had been used with the optical pyrometer there would probably have been no question concerning the use of nonblack bodies for a high temperature intercomparison. All that is necessary to make such an intercomparison valid is for the screen that is used in the eyepiece to be sufficiently monochromatic so that the different observers will get the same measured brightness by the use of the screen. It has been found[5] that with such red glass screens as were used in this work observers agree very well in their measurements.

When the brightness temperature of a source is measured by means of an optical pyrometer with a colored glass screen before the eyepiece, what is really measured is the brightness of the source as observed through the screen. This measured brightness corresponds to a certain temperature, say T, if it

[2] J.O.S.A. **5,** 494 (1921).
[3] Astrophys. J. **42,** 294 (1915).
[4] J.O.S.A. **10,** 35 (1925).
[5] Astrophys. J. **49,** 242 (1919).

is obtained from measurements on a black body. For this reason this brightness of a nonblack body is said to correspond to a brightness temperature, S, where $S = T$. The idea of a brightness temperature of a nonblack body as applied to a measured brightness corresponds to a definite narrow wave-length interval and in general a different brightness temperature is obtained when a different wave-length interval is used. If the brightness of a nonblack body that is measured for the wide wave-length band transmitted by the glass screen in the eyepiece of the pyrometer is to be interpreted as a brightness temperature S, to what wave-length is it to be ascribed? The brightness temperature S must be ascribed to a wave-length interval such that the energy emitted by a black body per unit area for temperature T will be equal to that of the source studied for the same wave-length. It has been shown[6] that the brightness temperature of a nonblack body that has been measured with a so-called monochromatic screen in the eyepiece of the pyrometer is to be ascribed to the effective wave-length between the brightness temperature obtained and the corresponding color temperature of the nonblack body. Thus if a series of measured brightness temperature of a nonblack body are ascribed to different wave-lengths they should be reduced to the same wave-length for comparison. With a good red glass screen this error is slight but the correction should be made for accurate work.

From Wien's equation and the conditions that hold at color match the following relation can be shown to hold between two brightness temperatures (S_1 and S_2) and the wave-lengths (λ_1 and λ_2) to which they correspond.

$$1/S_2 = \lambda_2/\lambda_1(1/S_1 - 1/T_c) + 1/T_c$$

where T_c is the color temperature corresponding to the brightness temperature s.

For a comparison of the result obtained in the different laboratories certain other factors must be taken into account to reduce all measurements to the same basis. The common basis taken for this purpose is the one adopted by the General Electric Company for use in its laboratories.[7] This temperature scale is based upon the assumption of Wien's equation with c_2 taken as 14330 μ deg.[8] and upon the melting point of gold taken as 1336°K, i.e., degrees Centigrade+273 degrees. On this scale the melting point of palladium has been found to be 1829°K. For convenience in calibration of optical pyrometers, a black body held at the melting point of palladium is used as a point of reference.

Since the red glasses used as monochromatic screens in the various laboratories did not have the same spectral transmission, the brightness temperatures obtained were not all ascribed to the same wave-length. Thus a small correction had to be made to reduce them to the same wave-length.

Since the Laboratories that took part in this intercomparison all based their high temperature scale on the brightness of the black body at the melting point of gold, which was in each case taken as 1336°K, there is no correc-

[6] General Electric Rev. **20,** 752 (1917).

[7] General Electric Rev. **20,** 819 (1917).

[8] The value now used is 14320.

tion for variation of fundamental temperature. This leaves but two corrections that must be applied to the values of temperature as reported to reduce them to the same base.

The other reduction is made necessary since the different laboratories did not all use the same value of the constant C_2. If different values of C_2 are used in extrapolating temperatures from a standard temperature, T_1, by means of Wien's equation the following is the relation between the two C_2's and the resulting temperature

$$C_2(1/T_1 - 1/T_2) = C_2'(1/T_1 - 1/T_2').$$

The final values all reduced to the common basis are shown in Tables II and III. Both the Physikalisch-Technischen Reichsanstalt (Lamps D-3 &

TABLE II. *Results of intercomparison of temperature scales.*
$C_2 = 14330\mu$ deg.: $\lambda = 0.665\mu$: melting point of Au = 1336°K (Pd = 1829°K)

Lamp	Current	N. R. L. Oct. 1916	G. E. Lab. Schenectady	N. R. L. Nov. 1916	Bureau of Standards	N. R. L. April 1917
T-25-C	10.9	1826°K	1828°K	1826°K	—	—
	14.6	2214	2214	2215	—	—
	18.0	2518	2518	2516	—	—
T-16-B	5.3	—	—	1429	1431°K	1427°K
	6.8	1618	1613	1617	1619	1614
	8.6	1816	1811	1811	1813	1812
	11.8	2128	2116	2122	2122	2121
T-30-C	15.3	1813	1813	1813	1814	1813
	21.0	—	2307	2304	2302	2303
	27.5	2756	2752	2752	2762	2752

Lamp	Current	N. R. L. March 1916	University of Wisconsin C.E.M.	University of Wisconsin G.R.G.	N. R. L. July 1917
T-17-C	11.0	1810	1813	1816	1810
	14.6	2193	2197	2202	2196
	18.0	2499	2506	2516	2497
T-18-B	6.7	1599	1602	1605	1597
	8.8	1806	1816	1819	1807
	12.0	2105	2119	2123	2107

Lamp	Current	N. R. L. April 1920	N. P. L. April 1922	N. R. L. June 1922	Bureau of Standards Jan. 1923	N. R. L. Jan. 1923
T-77-B	5.2	1410°K	1403	1406	1401	1401
	6.7	1599	1596	1595	1596	1591
	8.5	1796	1794	1794	1792	1791
	11.7	2106	2106	2104	2105	2104
T-78-C	15.4	1825	1825	1826	1824	1828
	20.4	2262	2265	2266	2265	2269
	27.4	2746	2757	2753	2755	2755

P-8) and the Philips Glowlampworks (Lamps I, II, & III) prepared and sent to Nela Park special lamps for this intercomparison. The data on these lamps are also included in Table III. An inspection will show very good agreement. Some of the lamps did not remain as constant as might have been desired. It thus seems that a part of the small differences found is to be charged

TABLE III. *Results of intercomparison of the high temperature measurements with laboratories in Europe*
$C_2 = 14330\mu$ deg.: $\lambda = 0.665\mu$: melting point of Au = 1336°K (Pd = 1829°K)

Lamp No.	Current	Nela May 1928	P. T. R. July 1929 Apr. 1931	Nela Jan. 1930
181	14	1800°K	1800°K	1797°K
	21½	2402	2400	2393
	26	2696	2690	2692
182	14	1788	1798	1796
	21½	2388	2396	2388
	26	2682	2694	2682
183	14	1807	1800	1812
	21½	2408	2408	2416
	26	2704	2706	2712
184	14	1786	1794	1793
	21½	2394	2398	2391
	26	2689	2696	2687

Lamp No.	Current	Nela 1931	P. T. R. 1931
D-3[1]	9.750	1347°K	1339°K
	14.340	1862	1860
	19.670	2309	2303
	22.060	2474	2476
P-8[1]	9.200	1339	1337
	15.400	1859	1861
	22.900	2326	2321

Lamp No.	Current	Nela	Laboratoire Central
F-71-C	10	1441°K	1438°K
	12	1646	1648
	14	1817	1817
	16	1966	1971
	18	2112	2111
	10	1440	1939_5
F-74-C	10	1370	1380
	12	1591	1602
	14	1766	1773
	15	—	1850
	16	1916	1931
	17	—	2005
	18	2060	2071
	10	1371	1381.5

Lamp No.	Current	Nela Oct. 1923	Philips June 1924	Nela Aug. 1924
F-61-C	12	1584°K	1588°K	1582°K
	10	1301	1293	1302
	15	1898	1899	1898
	20	2300	2312	2295
	27	2758	2783	2760
	12	1579	1589	1579
F-75-C	10	1448	1450	1446
	12	1656	1657	1656

[1] Ribbon filament lamp from Physikalisch-Technischen Reichsanstalt.

TABLE III. (*continued*)

	14	1821	1820	1826
	16	1970	1979	1971
	18	2129	2119	2123
	10	1447	1449	1446
F-76-C	10	1326	1337	1327
	12	1550	1558	1551
	14	1724	1730	1727
	16	1875	1879	1874
	18	2016	2018	2014
	10	1324	1335	1325

Lamp No.	Current	Philips Oct. 1925	Nela Feb. 1926	Philips July 1926
I[2]	4.5	1353°K	1353°K	1355°K
	5.0	1530	1530	1527
	5.5	1670	1674	1675
	9.5	2459	2459	2468
	4.5	1352	1353	1353
II[2]	4.5	1235	1236	1232
	5.0	1443	1440	1440
	5.5	1607	1606	1611
	9.5	2445	2424	2442
	4.5	1233	1236	1233
III[2]	4.5	1345	1347	1348
	5.0	1535	1535	1537
	5.5	1674	1674	1676
	9.5	2467	2468	2465
	4.5	1348	1348	1348

Lamp No.	Current	Nela Sept. 1924	Osram June 1925	Nela Jan. 1926
F-116-C	9	1273°K	1268°K	1272°K
	10	1418	1413	1416
	12	1635	1634	1633
	14	1812	1812	1813
	16	1961	1968	1967
	18	2114	2116	2116
F-117-C	9	1375	1371	1374
	10	1501	1500	1503
	12	1710	1705	1708
	14	1884	1882	1884
	16	2041	2039	2043
	18	2192	2192	2193
F-114-C	10	1305	1302	1299
	12	1576	1576	1579
	15	1884	1885	1885
	20	2294	2296	2297
F-115-C	10	1322	1319	1324
	12	1596	1597	1598
	15	1913	1908	1905
	20	2322	2324	2318

[2] Wire filament lamp from Philips Glowlamp Works.

against the lamps rather than the Standard Scale. Certainly the agreement obtained for the high temperature scale is very good.

This intercomparison has been made possible by the kind coöperation of the men of the different laboratories that took part in the work and we want to express our appreciation to them for their help.

THERMOCOUPLES WHOSE ELEMENTS ARE LONGITUDINALLY AND TRANSVERSELY MAGNETIZED FERROMAGNETIC SUBSTANCES

By Stewart Seass
Fayerweather Laboratory of Physics, Amherst, Mass.

(Received August 3, 1931)

Abstract

A ferromagnetic wire is bent at right angles to form a square U-shaped conductor. If the two bends are kept at different temperatures and the section between the two corners is magnetized transversely while the portions leading from the right angles are longitudinally magnetized, an e.m.f. is set up between the bends. In the following paper, the values of this e.m.f. for different magnetic fields are shown. Also, the relations between this effect, discovered by Sir William Thomson in 1856, and an effect discovered by von Ettingshausen and Nernst, nearly thirty years later, are indicated.

Ross[1] has studied the thermal e.m.f. of nickel and iron wires when longitudinally and transversely magnetized portions of the same piece of wire are the elements of the thermocouple. The procedure was suggested by Sir William Thomson[2] and was essentially as follows: an iron or a nickel wire was bent into the form shown in Fig. 1 and the section, B – F, was placed

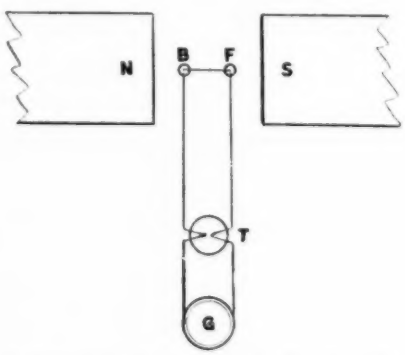

Fig. 1. Arrangement of thermo-electric circuit in Ross' work. *N-S* is the electromagnet. *T* is a thermos bottle to maintain constant temperature for the terminal junctions. *G* is the galvanometer.

between the poles of an electromagnet in such a way as to be longitudinally magnetized while the other portions were transversely magnetized. When the bends *B* and *F* were kept at a boiling and freezing temperature respectively, a thermal e.m.f. was developed in the wire which could be measured by a sensitive galvanometer. The direction of the e.m.f. in such a couple was, in general, from a transverse to a longitudinal magnetization through the hot

[1] Ross, Phys. Rev. **38**, 179 (1931).
[2] Thomson, Math. and Phys. Papers **2**, 267–307.

junction. For iron there was a small range of field strengths where the direction of the current was reversed.

The influence of a magnetic field upon thermal e.m.f.'s is in some unknown way associated with the changes in length which occur in ferromagnetic substances when they are magnetized.[3] Roughly, the change in length when an iron rod is magnetized longitudinally is just the reverse of what it is when magnetized transversely.[4] It was to be expected that the effect studied by Ross would be different if the section *B* to *F*, Fig. 1, were magnetized transversely and the other sections longitudinally.

The purpose of this study, therefore, is to see how the thermal e.m.f. would vary with the magnetizing force when the magnetic field was normal to the section B – F. As was to be expected the current was, in general, from transverse to longitudinal magnetization through the hot junction. This means that if the magnetic field in Ross' work were turned through 90° it would reverse the current in the wire since in both cases the direction of the e.m.f. is from transverse to longitudinal magnetization through the hot junction.

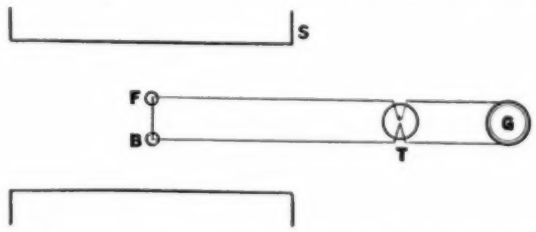

Fig. 2. Arrangement of thermo-electric circuit in Seass' work. *S* is the solenoid. *T* is a thermos bottle to maintain constant temperature for the terminal junctions. *G* is the galvanometer.

The nickel and iron wires used in this study were taken from the same samples as the iron and nickel wires used in Ross' work. Their chemical analyses are given in his paper.

In order that a magnetic field might be applied at right angles to the section *B* – *F* and parallel to the others, the electromagnet used by Ross could not be conveniently employed. A solenoid with a large inner diameter was, therefore, substituted as shown in Fig. 2. This solenoid had a constant of 34.03 gausses per ampere and was determined both by calculation and by a standard inductance. The length of the solenoid was 47 cm and the average radius of the 8 layers of windings was 16.8 cm. There were 1580 turns to the entire coil. The wire was wound on a Bakelite tube with wooden flanges at the ends.

The procedure for taking readings was to hold *B* and *F* steadily at 100°C and 0°C, respectively, while the magnetic field was varied, then exchange the temperatures of *B* and *F* and while holding these steady again observe the e.m.f.'s as the field was varied. The averages of these results are shown in Fig. 3. It will be noted that the maxima and minima do not appear which

[3] Smith, Ohio State Univ. Bul. No. 20, Exp Station. Aug. 1921; Williams and Sanderson, Phys. Rev. **37**, 309 (1931).

[4] Williams, Phys. Rev. **4**, 498 (1914).

occurred in Ross' work. Of course it was not possible to get such field strengths as Ross did with his electromagnet, but so far as the field strengths were carried this effect is not a complete reversal of the former. The change in length due to a transverse field is also not an exact reversal of the change due to a longitudinal magnetic field.

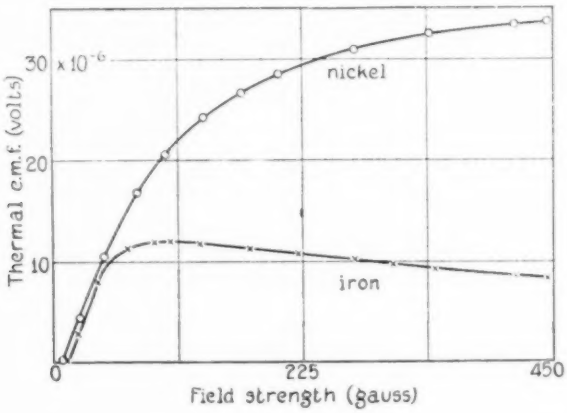

Fig. 3.

In 1886 von Ettingshausen and Nernst[5] discovered what they called a new effect among the various thermomagnetic phenomena. They found that if a plate of bismuth has a heat gradient from one end to the other as shown in Fig. 4, and a magnetic field is applied normal to the plate and to the direction of flow of heat, a longitudinal e.m.f. will be set up in the plate, as for instance, between the points *B* and *F*, Fig. 4. If the effect studied in this

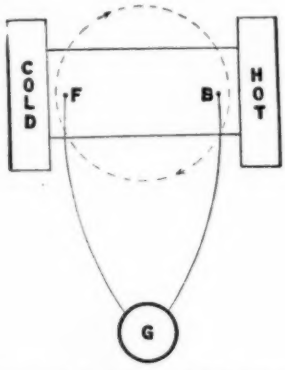

Fig. 4. Arrangement of apparatus for the von Ettingshausen-Nernst experiment. *G* is the galvanometer.

paper is compared with the von Ettingshausen-Nernst effect, it will be observed that there are many similar conditions which will warrant special consideration.[6] (1) Both effects have a heat gradient in a conductor normal to a

[5] Von Ettingshausen and Nernst, Wied. Ann. **29,** 343 (1886).
[6] Williams, Science **74,** 75 (1931).

magnetic field. (2) The von Ettingshausen-Nernst effect has not been found in conductors other than ferromagnetic bodies unless in highly diamagnetic substances with very specific crystal orientation. The effect, first proposed by Thomson, is found only in ferromagnetic substances and has yet to be tried out in conductors like bismuth.

Unfortunately, observers of the so-called von Ettingshausen-Nernst effect have studied the ferromagnetic conductors without regard to the effect found by Thomson. This has introduced all sorts of confusion because Thomson made it very clear that the arrangement of the conductors leading from B and F to the galvanometer is very important.

The fact that the von Ettingshausen-Nernst effect has been found only in ferromagnetic conductors or bodies like bismuth might very well raise doubt as to the existence of such an effect as distinct from the effect found by Thomson. A very careful study of this effect is now being undertaken in bismuth to see if a definite answer may be had to this very important question. In this present study copper, a nonferromagnetic substance, was studied and no e.m.f. was discovered.

Thanks are due Professor S. R. Williams for suggesting this problem.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

One-Dimensional Problems in Quantum Mechanics

In studying the results to be obtained from the approximation of potential functions by step-functions a way of treating the one-dimensional problem has been found which seems somewhat unusual. That it is altogether new is doubtful, but I have not been able to locate it in any of the familiar treatises on differential equations. The type form of Schrödinger's equation is

$$(d^2\psi/dx^2) + 4\pi^2\alpha^2(x, E)\psi = 0 \qquad (1)$$

where $\alpha^2(x,E) = 2m[E - V(x)]/h^2$. If $\alpha = \text{const.}$ then ψ is given by

$$\psi = c_1 e^{+i2\pi\alpha x} + c_2 e^{-i2\pi\alpha x} \qquad (2)$$

where c_1 and c_2 are constants. If α is not constant then we can try to solve (1) by treating c_1 and c_2 as well as α as functions of x. This is not quite the usual variation-of-constants method since we put a function of x in the exponential as well as vary the c's. The point to the scheme is that one can find differential equations for $c_1(x)$ and $c_2(x)$. These are

$$\begin{aligned}(dc_1/dx) &= A_1(x)c_1 + A_2(x)c_2 \\ (dc_2/dx) &= A_2^*(x)c_1 + A_1^*(x)c_2\end{aligned} \qquad (3)$$

with

$$\begin{aligned}A_1(x) &= -[d\ln\alpha^{1/2}/dx](1 + i4\pi\alpha x) \\ A_2(x) &= [d\ln\alpha^{1/2}/dx]e^{-i4\pi\alpha x}.\end{aligned}$$

The exact method by which these formulas were derived will not be given here. Using (3) it can easily be verified that (2) satisfies (1), and since the solution of (3) requires just as many arbitrary constants as does that of (1), (2) will be the general solution of (1). Again using (3) one can readily show that

$$(d\psi/dx) = i2\pi\alpha[c_1 e^{+i2\pi\alpha x} - c_2 e^{-i2\pi\alpha x}].$$

More interesting than this is the fact that the current turns out to be

$$I = (h\alpha/m)[\,|c_1(x)|^2 - |c_2(x)|^2] = \text{constant}, \qquad (4)$$

exactly as though α were constant. Thus (2) can be interpreted, *in general* as representing currents travelling to the right and to the left with varying amplitudes $|c_1(x)|^2$ and $|c_2(x)|^2$ respectively. Eq. (4) shows that the current lost from one beam is gained by the other. It is this general separation of the two beams which seems to be new.

One of the original hopes was that some general differential equation could be found for the reflection coefficient R. This can be done, but only in an unsatisfactory manner. The natural definition of R is $R(x) = |c_2(x)|^2/|c_1(x)|^2$ so that $R(x)$ can be interpreted as the reflection coefficient for all of the potential curve lying to the right of x. This presupposes that $|c_1| \to 1$ and $|c_2| \to 0$ as $x \to +\infty$ so that the flow becomes unidirectional at $x = +\infty$. This R satisfies the equation

$$[d\ln(1 - R)/dx] = [d\ln\alpha^{1/2}/dx]\cdot(z + z^*)$$

where $z = (c_2/c_1)e^{-i4\pi\alpha x}$ satisfies the differential equation

$$(dz/dx) = [d\ln\alpha^{1/2}/dx](1 - z^2) - i4\pi\alpha z.$$

This is unsatisfactory since z involves c_1 and c_2 linearly while R involves only $|c_1|^2$ and $|c_2|^2$.

E. L. Hill

Department of Physics,
University of Minnesota,
September 1, 1931.

Hyperfine Structure and Nuclear Moment of Rhenium

The Re I spectrum has been photographed in the range 3000A to 6800A with spectrographs of high resolving power at the Mount Wilson Observatory, and the majority of lines are found to be complex, having 2 to 6 components. The most striking lines are those

which have "flag patterns," with both separations and intensities diminishing from one side of the pattern to the other. Such lines are undoubtedly transitions between two complex levels one of which has a much larger hyperfine structure than the other. For example the lines $5d^5 6s^2\ {}^6S - 5d^5 6s 6p\ {}^6P$ (3452, 3460, 3465A) and $5d^5 6s^2\ {}^6S - 5d^5 6s 6p\ {}^8P$ (4889, 5276A) are of this type and one would expect the interaction between the nuclear moment and the extranuclear electrons to be much larger for the P states. Other lines for which the j-values of both levels are as high as $5\frac{1}{2}$ and which also have flag patterns, show only 6 components.

According to recent work of Aston, rhenium has two isotopes with mass numbers 185 and 187 which are present in the ratio 1 to 1.62. If either of these isotopes had zero moment one would expect a marked increase in intensity in the neighborhood of the center of gravity of each pattern. However, the flag patterns all decrease regularly in intensity with decreasing separation, so that one may conclude that both isotopes of rhenium have the same nuclear moment, $2\frac{1}{2}(h/2\pi)$.

W. F. MEGGERS, Bureau of Standards
A. S. KING, Mount Wilson Observatory
R. F. BACHER, National Research Fellow,
California Institute
Mount Wilson Observatory,
August 28, 1931.

BOOK REVIEWS

Theoretical Physics. Vol. I. W. Wilson. Pp. x+332, figs. 80. Methuen and Company, Ltd., London, 1931. Price 21 s.

Following the general principle of supply and demand the last two or three years have seen the publication of a slowly increasing number of texts on general mathematical physics. While German and French students have always had numerous good books from which to choose, American and English students have been very limited in this respect. Just why this has been so is not clear. In America it has been too often true that the initial study of the mathematical theory has been delayed until the graduate years, undoubtedly due, to some extent at least, to the lack of adequate texts. With the rapidly increasing technical requirements in all departments of research, it is certainly to be desired that the study of the general theory be started as soon as possible. The existence of good texts such as the one under review should remove one of the few possible objections to such a raising of the standards of the undergraduate training.

The projected plan for this work of Professor Wilson calls for three volumes, of which only the first has appeared. Vol. I covers the general topics of mechanics and heat, Vol. II is to be on electromagnetism and optics, while Vol. III is to take up relativity and quantum dynamics. In this first volume an astonishing number of topics is covered. The author has a style which combines at once brevity and clarity, and the developments will require close attention from the reader. The material given is quite standard and, with supplementary lectures and discussions, should form the basis for a first class preliminary study of theoretical physics. The developments are straight-forward and no attempt is made to employ short cuts and trick solutions which cause students so much trouble.

The range of subjects covered is too large to permit more than a brief outline. After a preliminary chapter on vector and tensor analysis, and the thorems of Green, Gauss, and Fourier, the dynamics of particles and rigid bodies is developed sufficiently to include a fair amount of the theory of the Lagrangian and the Hamilton-Jacobi equations. Chapters of wave propagation, elasticity, hydrodynamics, and the motion of viscous fluids cover the problem of nonrigid continuous media. The advantages of the vector notation are here clearly evident. As an interesting pedagogical innovation of which the reviewer highly approves, kinetic theory and statistical mechanics are placed before thermodynamics. The clear mental picture afforded by the former does much to help out the formalism of the latter.

One may hope that the publishers will see fit to sell the complete set of three volumes at a considerably reduced price to students when it has appeared.

E. L. Hill
University of Minnesota

Handbuch der Astrophysik, Band III, Zweite Hälfte: Grundlagen der Astrophysik, Dritter Teil. Pp. 352+viii, 131 Figs. Julius Springer, Berlin, 1930. Price 62 marks.

The careful partitioning in the title of the volume suggests the student whose rendition of Caesar's "Gallic Wars" began "All Gaul is quartered into three halves"!

The first article (128 pp.) is by Grotrian, and is entitled *Gesetzmässigkeiten in den Serienspektren*. It is essentially an abbreviated edition of his well-known "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei, und drei Valenzelektronen," giving about half as many energy-diagrams as the latter, as those for less common spectra have been eliminated. In a few instances new material has been added, as, for instance, the work of Edlen and Ericson on the spectra of Li^{++} and Be^{+++}.

The second monograph (135 pp.) is by Laporte, and is called the *Theorie der Multiplettspektren*. This fulfills a distinct need, for it is the most complete and up-to-date available diagnosis of complex spectra, as more complicated cases are cited than in the standard works of Hund and of Pauling and Goudsmit. It is good to see some attention again given to the "vector

model," for in my opinion, classical analogues based on this model are quite as instructive as those achieved by "matter-waves" and the like. A notable feature of Professor Laporte's article is that it considers energy levels in the intermediate cases between j-j and Russell-Saunders coupling, as it summarizes recent work by Houston, Goudsmit, Slater, and others. Intensities, however, are considered only in the limiting cases. The relations of spectra to the long periods of the Mendeleeff table and to magnetism are discussed. Finally a fifteen page bibliography, with a supplement at the end of the volume, is appended documenting recent articles (1926–1930) on the assignment of terms to individual atoms possessing complicated spectra. It is to be regretted that Professor's Laporte's monograph is not available as a separate volume and in English. The most serious criticism which might be advanced is that the various "sum-rules" and "stability laws" are presented in much too empirical a fashion, without showing that they are immediate and easy consequences of the fundamental ideas of quantum mechanics (invariance of the diagonal sum, or spur, the unitary character of transformation matrices, etc.). However, the author can scarcely be blamed for this omission, for I understand that he was virtually under oath not to use any matrices, simply because they are treated in another volume of the handbook. These days, this restriction seems just about as sensible as it would be to ask him to omit the word "the" because it is used in the other volumes.

Molecular spectra are both more complicated and more prolific than atomic spectra. There are, for instance, 922 conceivable diatomic molecules, as compared to 92 atoms. Nevertheless, the article by K. WURM on *Bandenspectra* contains only 64 pages, and is thus considerably shorter than the sections on atomic spectra. Possibly this brevity is to be justified on the ground that most stars are too hot for molecules. It is, of course, impossible for Dr. Wurm to discuss the fine details of molecular spectra in such a short space, but he does give a straightforward presentation of many of the fundamental features, including such topics as predissociation, the Franck-Condon principle, and intensity formulas. A quite extensive bibliography is included on individual molecular spectra.

It is something of a shock to find that a large volume devoted hitherto to spectroscopy terminates in an interesting 18 page article by MILNE, on the *Theory of Pulsating Stars*. Perhaps this is to remind us that the handbook is aimed to be one of astrophysics rather than pure physics!

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Die Grundlagen der Quantenmechanik, Zweite Auflage. DR. A. MARCH, viii+293 pp. Barth, Leipzig, 1931. Price 26 marks.

The author of this book has tried to give a "consequent treatment of the quantum mechanics from the statistical point of view," whereby especial attention has been paid to making the presentation understandable.

The uncertainty principle is discussed at the very beginning, even though historically it appeared as a by-product of the theory, and one which must be handled with care. After the introduction of the concept of a deBroglie wave, one is made acquainted with the wave mechanics of a single particle. It is shown how calculations in momentum space may be made, and an elementary account of transformation theory is given. The discrete spectrum of the hydrogen atom is discussed, but no treatment of the continuous spectrum is included. Such an omission is perhaps in line with the endeavor to give as elementary a treatment as possible, but the reviewer feels that this detracts from the worth of the book to a serious student.

The account of the matrix mechanics is quite readable, as is the section on the causality principle. After a chapter on perturbation theory, the many-body problem is taken up. The helium atom, the Fermi statistics, and the Bose statistics are discussed. In the last chapter, the wave-field theory, as it existed before the work of Heisenberg and Pauli, is presented.

The treatment of the many-body problem is woefully inadequate, and practically no mention of electron spin is made.

To beginners with a knowledge of German, the book may be recommended as containing a clear exposition of some of the elementary ideas. The research student, however, will probably find it unsatisfactory because of the very limited scope of the contents.

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Elektronen-Interferenzen, edited by P. DEBYE. Leipziger Vorträge 1930. pp. 85+vi; 35 figs. one table. S. Hirzel, Leipzig, 1930.

This is a collection of seven papers presented at a symposium, the third of its kind, held at the University of Leipzig in the summer of 1930. The subject under consideration was that of electron phenomena from the point of view of wave mechanics. The papers fall in two main groups, the first dealing with electron scattering and diffraction, the second with metallic conduction.

The first group includes a paper by Rupp on the inner potentials of crystals as revealed by the diffraction of low speed electrons, a paper by Wierl covering his work on the diffraction of electrons by molecular vapors, one by Mark in which he compares the diffraction of x-ray and electrons by crystals with special reference to Bethe's treatment of the latter phenomenon, and one by Mott on the form factors of atoms for electron scattering.

The second group begins with a paper by Grüneisen on the interpretation of the temperature variations of electric and thermal conductivity in metals in terms of wave mechanics and Fermi statistics. This is followed by one by Block in which he considered how the present theory is to be modified to allow for mutual action between conduction electrons. The last paper is by Peierls and deals with the conductivity of metals in strong magnetic fields.

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Handbuch der Experimentalphysik, Band XXIII, 2 Teil, **Phosphoreszenz und Fluoreszenz** (2 Teil) von P. LENARD, F. SCHMIDT, UND R. TOMASCHEK; **Lichtelektrische Wirkung** von P. LENARD UND A. BECKER. (Akademische Verlagsgesellschaft m.b.H. Leipzig 1928). Price 72 marks.

The first part of this volume concludes the discussion of phosphorescence and fluorescence to which the whole of the previous volume in the series was devoted. The second part, comprising over 500 pages, is a comprehensive summary of the field of photoelectricity. The scope of the work is indicated by the list of chapters: I, Fundamental Investigations; II, Photoelectric Effects at the Surfaces of Metallically Conducting Bodies in Vacuum; III, Photoelectric Effects at Conducting Surfaces in Gases; IV, Photoelectric Properties on Nonmetallic Solids and Liquids; V, Photoelectric Effects in Gases; VI, Technique and Applications. The first chapter, by Lenard and Becker, gives a good survey of the fundamental discoveries and conceptions in photoelectricity. The succeeding chapters are by Becker alone. One feels that the distribution of emphasis is somewhat unfortunate. Too much space is given to the description of many of the early experiments. In order to make a book of this sort as comprehensive as possible, it is of course desirable to refer to practically all that has been published in the field. But it does not seem necessary however to have given a detailed description of the technique of so many of the earlier experiments. By curtailing the discussion of the earlier experiments and devoting the space set free to the more recent investigations, the usefulness of the volume would have been increased. There is hardly any discussion of photoelectric theory; this however may have been deliberate in a series on experimental physics. It is surprising that, in the section on the velocities of photoelectrons, the author should have omitted all discussion of the important and significant relations between contact differences of potential, surface work functions, and stopping potentials. The last chapter—on practical applications—is of very little use to present day workers in the field, for, out of the 41 papers referred to, there are only two that bear a date after 1920!

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